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Oxidation of Vacuum Residue with the Addition of Crumb Rubber

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Abstract

The actual problem of the oil refining industry is to improve the process of oxidation of heavy oil residues and the properties of oil bitumen. One way to solve the problem is to add modifiers. The addition of modifiers leads to an intensification of the oxidation process and an increase in the characteristics of the bituminous binders. The work aims to study the effect of adding rubber crumb on the process of vacuum residue oxidation and the properties of the obtained rubber-bitumen binders (RBB). The influence of the size of crumb rubber and its content, the mixing stage and oxidation modes on the properties of rubber-bitumen binders are determined. Vacuum residue from the Omsk oil refinery was used as a raw material, which was modified with crumb rubber with a dispersion of 0.6–1.0 mm and less than 0.6 mm. The novelty of the research is the addition of crumb rubber to the vacuum residue and the oxidation process to obtain bitumen. The product of vacuum residue oxidation for 2 h at 260 °C with preliminary mixing of 2 wt.% crumb rubber with particle sizes less than 0.6 mm at 180 °C and additional mixing of 8 wt.% crumb rubber after oxidation corresponds to the brand of rubber-bitumen binder RBB 60/90. The rubber-bitumen binder is characterized by high elasticity and low Fraas point. Prepared asphalt concrete mixture based on RBB corresponded to type B according to physical and mechanical parameters. The complex shear modulus of the samples decreases with the temperature increase. Short-term aging resulted in increased shear modulus for all samples.

1. Introduction

Improving the quality of oil bitumen is an actual problem due to the increase in the volume of their consumption and the increase in the requirements for their quality. One of the effective ways to improve the quality of petroleum-based binders is the introduction of modifying additives of various nature into their composition at different stages of production [1].

In world practice, polymer-bitumen binders are widely used, which are produced by modifying bitumen with various polymers. Even though the modification of bitumen with polymers improves the resistance to permanent deformation of bitumen and asphalt concrete mixtures, the lack of elasticity at low temperatures limits the use of this bitumen [2].

The addition of crumb rubber to the composition of bitumen, obtained by processing worn-out automobile tires, tubes and other waste rubber products, is a promising direction for modifying bitumen. In world practice, three methods of introducing crumb rubber into asphalt concrete mixtures are used: "dry", "wet" and the introduction of crumb rubber directly into the asphalt concrete mixture [3].

The review [4] considered the possibility of using crumb rubber in hot mix asphalt to improve rutting resistance and create pavements with greater durability. The technology of adding crumb rubber to asphalt concrete mixtures makes it possible to reduce the thickness of the pavement layer but has

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disadvantages associated with the need for mixing equipment and its high cost and the complexity of developing the design of an asphalt concrete mixture [5].

The addition of crumb rubber by a dry method affects the composition of the asphalt mix and its characteristics [6–7]. The stability and density of the mixture decrease with the increasing content of crumb rubber. The addition of crumb rubber, especially with a smaller size, showed better resistance to rutting. This is due to the partial interaction between the rubber and bitumen particles, which simultaneously act as an elastic filler in the mixture.

The essence of the "wet" method is the introduction of crumb rubber into liquid bitumen and effective homogenization of the system at temperatures of 150–250 °C [8]. The disadvantages of this method are the need to use finely dispersed crumb rubber, which has a high cost, as well as a strong influence on the properties of the composition of homogenization modes and characteristics of the original crumb.

The content of rubber in the modified bitumen should not exceed 20% of the weight of the bitumen [9]. The addition of rubber reduces the softening point and plasticity, while with the addition of styrene-butadiene-styrene copolymer (SBS) these values increase compared to the original bitumen. With the addition of devulcanized rubber, the effect on the properties of bitumen is reduced, since the rubber is uniformly dispersed, but the bitumen loses its elasticity [9–10].

In the scientific publication [11], four types of crumb rubber were introduced into bitumen and its properties were studied. Natural rubber increased the stiffness of the bitumen and improved performance at high temperatures, but the bitumen also became brittle at low temperatures.

In the publication [12], the effect of crumb rubber on the elastic modulus and resistance to deformation of petroleum bitumen was studied. Crumb rubber with a particle size of 0.6 mm was added to the asphalt mix in an amount of 5 to 20% at the temperature of 177 °C. The addition of crumb rubber improved the penetration index, which led to a decrease in temperature sensitivity, a significant increase in the viscosity of the bitumen and an expansion of the temperature range of viscoelasticity.

Recycled rubber [13] as an additive to bitumen improved its properties by reducing temperature sensitivity. The addition of crumb rubber to bitumen improved the resistance to rutting and permanent deformation of the road surface (due to an increased viscosity), reduced fatigue cracking, and increased the resistance of asphalt concrete to aging.

The properties of bitumen with the addition of crumb rubber under various conditions have been studied [14]. Bitumen with a crumb rubber content of 15% showed the highest softening point, which was 61 °C, while penetration was 42 dmm. However, the authors [14] limit the content of crumb rubber to 10% based on the penetration value to avoid excessive hardening of the modified bituminous binders. Excessive hardening of the bituminous binder can lead to cracking.

Thus, crumb rubber is one of the effective modifiers of bituminous binders and a large number of studies have been carried out on their effect on the properties of bitumen and road surfaces. The optimal content of crumb rubber in a mixture with bitumen is proposed in an amount from 3 to 20 wt.%. Crumb rubber acts as a modifier that affects the structure of bitumen components by controlling phase transitions and changing the molecular-dispersed state of bitumen. However, all of these studies consider the addition of crumb rubber to the finished bitumen or asphalt mix and the further use of rubber-bitumen binders.

In these methods, crumb rubber is not mixed with bitumen to a homogeneous state, since it does not dissolve in the mixture under normal processing conditions and does not form a continuous polymer network [15].To effectively combine bitumen with crumb rubber, it is necessary to improve the process of oil residue oxidation. The introduction of modifying additives into the vacuum residue before oxidation leads to a change in the ratio of the components of the dispersed phase and the dispersed medium, which affects the rate of the oxidation process [16, 17].

In this paper, crumb rubber modification is carried out not on paving bitumen, but on bituminous raw materials, such as vacuum residue. The vacuum residue is one of the suitable materials for producing heavy hydrocarbons [18]. The work aims to study the effect of adding crumb rubber on the process of vacuum residue oxidation and the properties of the resulting rubber-bitumen binders.

2. Materials and Methods

2.1. Vacuum residue

Vacuum residue from the Omsk Oil Refinery was chosen as the bituminous raw material, which is used in "Asphaltobeton 1" LLP (Almaty) to produce

Table 1
Group and fractional composition of vacuum residue

Indicator	Vacuum residue
Oil content, wt.%:	
paraffin-naphthenic	25.9
light aromatic	9.9
medium aromatic	2.8
heavy aromatic	18.1
Resin content, wt.%:	
neutral resins	11.2
acidic resins	20.3
Asphaltene content, wt.%	11.8
Fractions of liquid distillate, wt.%:	
beginning of the boiling point – 180 °C	7.0
200–350 °C	32.9
350 °C – end of the boiling point	60.1

oxidized bitumen. As shown in Table 1, the vacuum residue contains a large amount of paraffin-naphthenic (25.9%) and heavy aromatic oils (18.1%). The total content of resins (31.5%) and asphaltenes (11.8%) are also significant. The vacuum residue has a density of 957.0 kg/m^3 at 20 °C, analysis of the fractional composition showed that the content of light distillates was 39.9%.

2.2. Crumb rubber

Crumb rubber produced by "Q-Recycling" LLP (Almaty), of various dispersions was used as a vacuum residue modifier: particle sizes of 0.6–1.0 mm and less than 0.6 mm. The technical characteristics of crumb rubber are given in Table 2.

2.3. Installation and oxidation process

A laboratory device was made for the producing oxidized modified bitumen, its scheme is shown in Fig. 1. The steel cylindrical reactor is heated in a furnace, the heating temperature is fixed by a thermostat. An air inlet is connected to the reactor, which is mounted in the form of a spiral on the walls of the reactor, so the air for oxidation also enters a heated state. The airflow is controlled by pre-calibrated rotameters. The process temperature is measured by thermocouples located in the reactor and the furnace.

The vacuum residue is poured into the reactor, then, depending on the mass of the vacuum residue, from 2 to 15 wt.% crumb rubber is added. At a temperature of 100–120 °C, the air supply compressor is switched on, the air supply rate is 8–10 l/min. The temperature of the oxidation process is 260 °C, and the oxidation time is from 2 to 7 h.

The process of oxidation of vacuum residue with the addition of crumb rubber was carried out under several modes:

1) crumb rubber of various dispersions was added to the vacuum residue and oxidation was carried out at 260 °C;

2) crumb rubber was added to the vacuum residue and stirred at the temperature of 180 °C for 0.5–1 h, then oxidation was carried out at 260 °C;

3) crumb rubber was added to the vacuum residue and mixed at the temperature of 180 °C for 0.5 h, then oxidation was carried out at 260 °C for 2 h, after which the oxidation product was mixed with crumb rubber for 0.5 h.

Table 2
Specifications of crumb rubber produced by "Q-Recycling" LLP

Indicator	Test results of crumb rubber	Requirements ST RK 2028-2010
Mass fraction of cord fiber residues (viscose and nylon), %	0.02	no more 1.0
Mass fraction of rubber sifted through a sieve with a mesh of 1.4,%	100.0	at least 100.0
Mass fraction of rubber sifted through a sieve with a mesh of 1.0,%	92.59	at least 90.0
Mass fraction of rubber sifted through a sieve with a mesh of 0.63,%	50.0	at least 50.0
Mass fraction of rubber sifted through a sieve with a mesh of 0.315,%	8.47	not standardized
Mass fraction of ferrous metal particles (after magnetic separation), %	not detected	no more 0.005

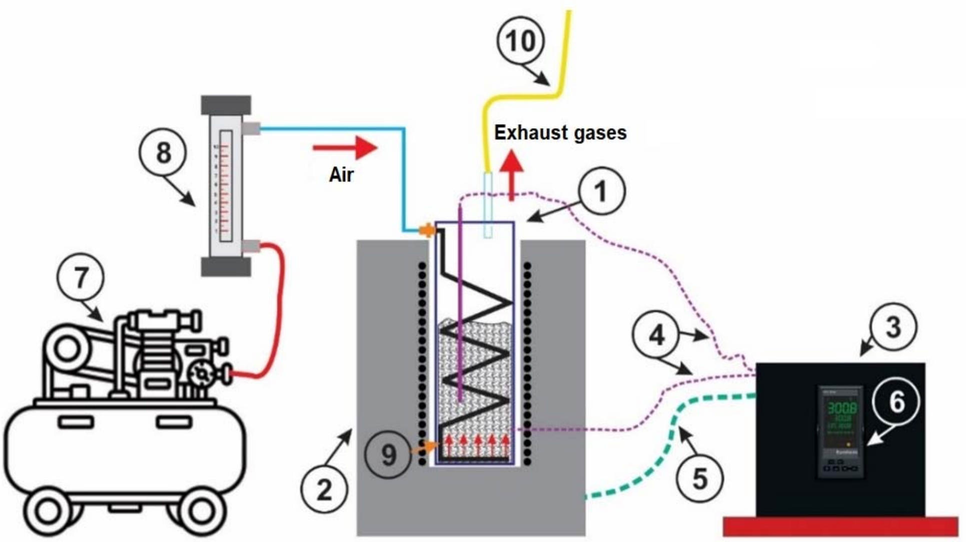

Fig. 1. Scheme of the installation for the oxidation of vacuum residue: 1 – a cylindrical steel reactor; 2 – an electric tube furnace; 3 – a temperature controller with a temperature controller; 4 – thermocouples; 5 – power supply; 6 – temperature controller; 7 – compressor; 8 – airflow meter; 9 – branch pipe for air supply; 10 – the flow of exhaust gaseous products.

2.4. Group composition

The group composition of the vacuum residue was determined by the adsorption-chromatographic method of Marcusson, consisting of the precipitation of asphaltenes with petroleum ether. To separate oils and resins, their different ability to be sorbed by silica gel is used.

2.5. Fractional composition

The fractional composition of the vacuum residue is determined by the ARN-2 oil distillation apparatus by the State standard 11011-85.

2.6. Conventional characteristics

To establish the optimal conditions of the oxidation process, the main physical and mechanical characteristics of the oxidation products were determined: the depth of penetration of the needle (penetration) at 25 °C and the softening point along the ring and ball (R&B). Penetration characterizes the plasticity of the material, and softening point – the ability of bitumen to maintain its properties at elevated temperatures. The penetration at 25 °C of the oxidation products was determined with an APN-360MG4 penetrometer by the Standard of the Republic of Kazakhstan 1226-2003. The softening point of the samples was determined by the "ring and ball" method on an IKSH-MG4 device by the Standard of the Republic of Kazakhstan 1227-2003.

The product of oxidation of vacuum residue with the addition of crumb rubber, obtained under the optimal mode, was tested to determine all the standard physical and mechanical characteristics. Based on it, an asphalt concrete mixture was prepared, the physical and mechanical properties of which were also determined by standard methods.

2.7. Dynamic shear rheometer

The mechanical characteristics of the samples at temperatures from 1 to 70 °C were measured by a dynamic shear rheometer according to the standard [19]. Samples in the form of a circular plate with a diameter of 25 mm and a thickness of 1 mm were tested for sinusoidal variable deformation with an amplitude of 12% and a frequency of 10 rad/s. Before the test, the samples were kept at a specified temperature for at least 10 min. Based on the test results, shear stress τ and shear strain γ were measured. The value of complex shear modulus G* of the samples is calculated by the formula [20]:

$$G^* = (\tau_{max} - \tau_{min})/(\gamma_{max} - \gamma_{min})$$

where τ_{max}, τ_{min} are the maximum and minimum shear stresses, respectively; γ_{max}, γ_{min} are the maximum and minimum shear strains, respectively.

Short-term aging of samples was carried out in a special rolling thin film oven (RTFO) according to the standard [21], which models bitumen aging during the preparation, transportation, laying and compaction of an asphalt concrete mixture. The samples were kept in the oven at the temperature of 150 °C for 75 min, where the uniform oxidation of the sample is ensured by the continuous formation of its thin layers under the influence of heat and air.

2.8. FTIR spectroscopy

The FTIR spectrometer of the model Cary 630 (Agilent Technologies, Inc., Malaysia) was used for infrared (IR) spectroscopy analysis of the vacuum residue and products of its oxidation. All spectra were recorded within wave numbers from 600 to 4000 cm^{-1}.

3. Results and discussion

This section presents the results of vacuum residue oxidation under different technological conditions and modifications with different amounts of crumb rubber. Among the important quality indicators of oxidized bitumen, characterizing their commercial properties, are penetration and softening point. Penetration indirectly characterizes bitumen stiffness and it is inversely proportional to viscosity. The softening point indicates the area of plastic deformations, corresponding to the transition of a substance from an amorphous state to a viscous-flowing one. Figure 2 shows the dependences of penetration and softening point of oxidation products with the addition of crumb rubber with particle sizes of 0.6–1.0 mm in an amount of 15 wt.% of the vacuum residue oxidation time. As can be seen from the figure, the penetration of products decreases and the softening point increases with the increase in the oxidation time. The penetration of the products decreased from 204 to 41·0.1 mm, the softening point increased from 39 to 58 °C during the oxidation time from 3 to 7 h. At the same time, products that were suitable for determining these characteristics were obtained after oxidation from 3 to 7 h and with the addition of crumb rubber in the amount of 15 wt.%. Oxidation of vacuum residue with the addition of crumb rubber less than 15 wt.% did not lead to satisfactory results. It should be noted that when adding large particles of crumb rubber with a size of 0.6–1.0 mm, their complete dissolution and uniform distribution of crumb particles in the volume of the vacuum residue is not achieved. In this regard, subsequent experiments were carried out with the addition of crumb rubber up to 0.6 mm in size.

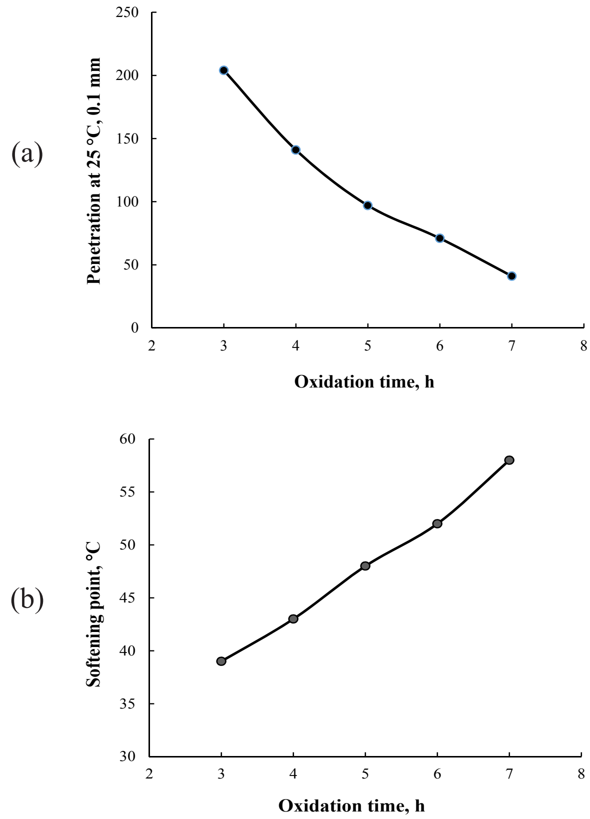

Fig. 2. Dependences of penetration at 25 °C (a) and softening point (b) of vacuum residue oxidation products with the addition of 15 wt.% crumb rubber (0.6–1.0 mm) from the duration of oxidation.

The dependences of the penetration and softening point of the oxidation products of vacuum residue modified with different amounts of crumb rubber with a particle size of up to 0.6 mm on the duration of oxidation are shown in Fig. 3. As can be seen from Fig. 3a, the penetration values of the oxidation products decrease with increasing process duration, but the process time oxidation was reduced to 4 h. The decrease in penetration from 220 to 36·0.1 mm and the increase in the softening point from 39 to 62 °C are observed during the oxidation time from 2.5 to 4 h. When adding crumb rubber to the vacuum residue in the amount of 5 wt.% curves of penetration change during oxidation of 3.5–4 h are located above the curve of the oxidation product of vacuum residue without the modifier. This is explained by the fact that a small amount of crumb leads to the increase in the plasticity of bitumen. The same pattern is observed in the change in the softening point.

Figure 4 shows the dependence of the penetration and softening point of the vacuum residue oxidation products for 3 h with crumb rubber in particle sizes up to 0.6 mm. As can be seen, the

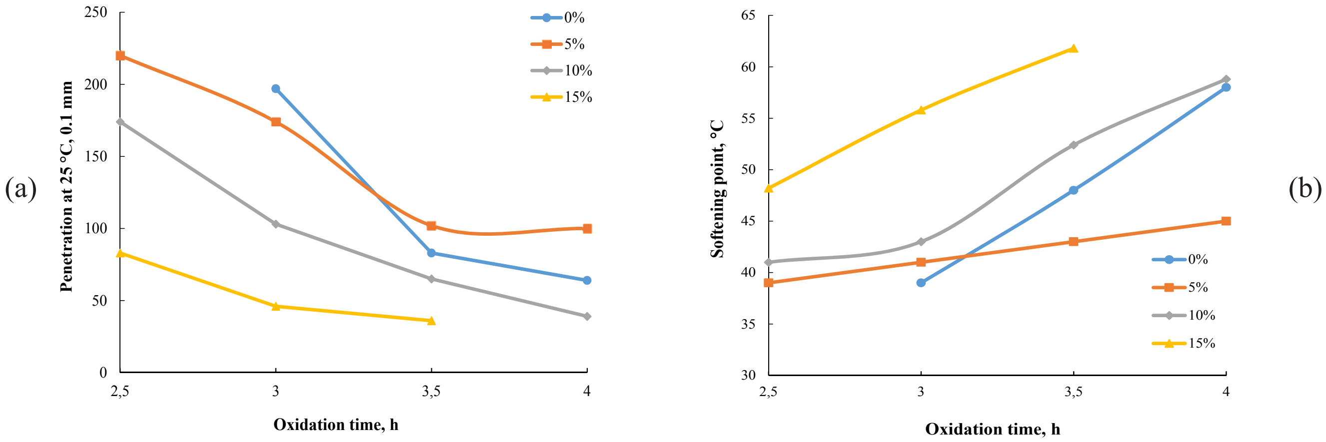

Fig. 3. Dependences of penetration at 25 °C (a) and softening point (b) of vacuum residue oxidation products on the processing time with the addition of various amounts of crumb rubber.

penetration decreases from 174 to 46·0.1 mm, and the softening point of the oxidation products increases from 41 to 56 °C with the increase in the amount of crumb rubber added from 5 to 15 wt.%. Compared with the results of the oxidation of vacuum residue with the addition of coarse crumb rubber (0.6–1.0 mm), in the case of the addition of crumb of small dispersion, to achieve the indicated values of penetration and softening point, it was possible to reduce the oxidation time by more than 2 times, i.e. from 7 to 3 h.

To improve the properties of bituminous binders, the oxidation process was further carried out with preliminary mixing of vacuum residue and crumb rubber at the temperature of 180 °C before oxidation. Pre-mixing allows getting a homogeneous system. Figure 5 compares the penetration and softening point of the vacuum residue oxidation products for 3 h with pre-mixing with different amounts of crumb rubber for 0.5 and 1 h. Oxidation products with the addition of 5 and 10 wt.% crumb rubber obtained with pre-mixing for 0.5 h, and with the addition of 5' and 10' wt.% – with stirring for 1 h. As can be seen from the diagram, there is an effect of the premixing stage on the physico-mechanical characteristics of the oxidation products. Pre-mixing led to a sharp decrease in penetration to (19–34)·0.1 mm, while the oxidation products of vacuum residue with the addition of 10 wt.% have higher penetration values than with the addition of 5 wt.%. The softening point of the oxidation products also increased sharply to 63–81 °C, while its value for products with the addition of 5 wt.% crumbs is higher than with the addition of 10 wt.%. This is explained by the fact that, compared with the usual technological regime, when the oxidation process occurred for 3 h, an additional pre-mixing stage was carried out here, which led to an increase in the duration of the entire process and a sharp change in penetration and softening point. In the

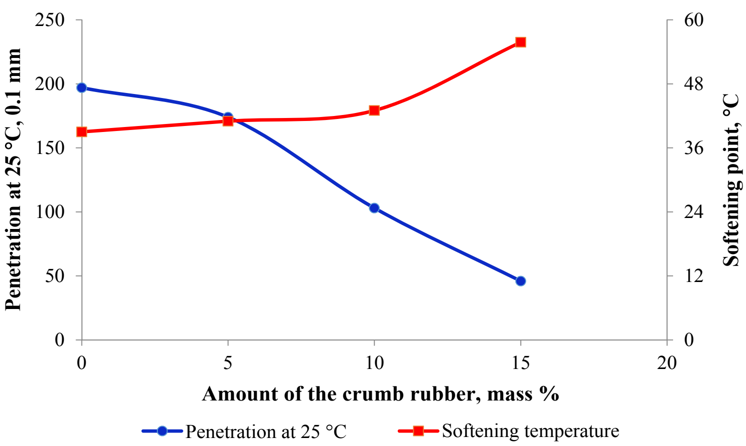

Fig. 4. Dependences of penetration at 25 °C (a) and softening point (b) of vacuum residue oxidation products for 3 h on the amount of the crumb rubber.

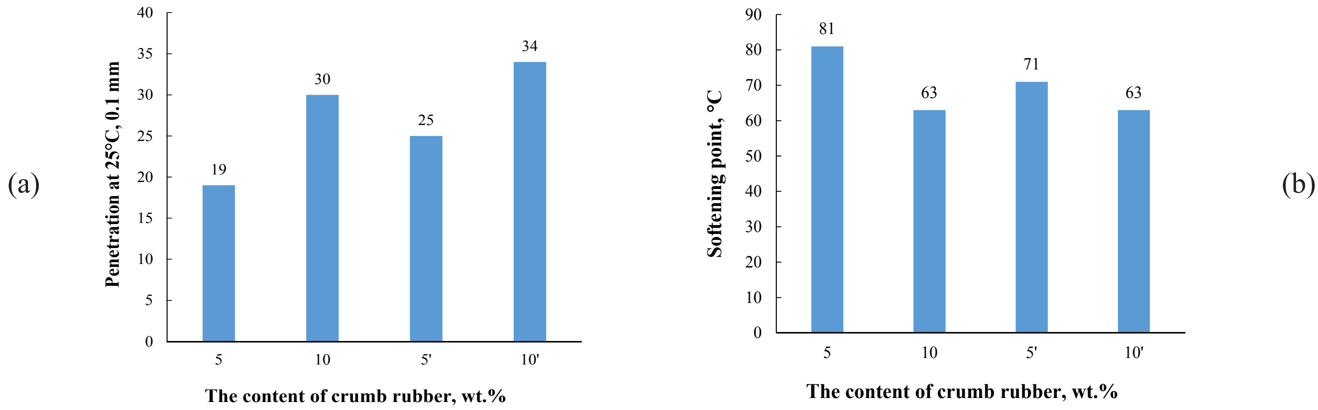

Fig. 5. Penetration at 25 °C (a) and softening point (b) of vacuum residue oxidation products for 3 h at various contents of crumb rubber.

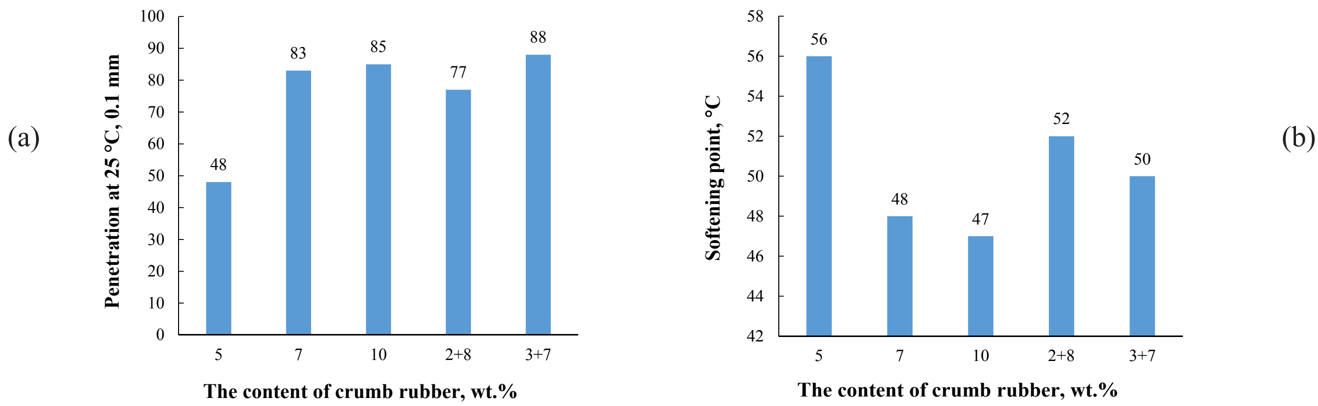

Fig. 6. Penetration at 25 °C (a) and softening point (b) of vacuum residue oxidation products for 2 h at various contents of crumb rubber.

process of mixing crumb rubber with vacuum residue, it interacts with light low-molecular fractions of vacuum residue, which leads to rubber swelling and leaching of soluble ingredients from it with the decrease in its mass [22].

Since the results of oxidation with preliminary mixing did not meet the requirements for standard normative indicators, subsequent experiments were carried out with preliminary mixing of vacuum residue with a reduced amount of crumb rubber 2–3% at a temperature of 180 °C for 0.5 h, then the oxidation process was carried out at the temperature of 260 °C for 2 h and additional mixing of 7–8% crumb rubber for 0.5 h after oxidation. In Fig. 6, the penetration and softening point of the oxidation products are presented in two modes: with preliminary mixing of the vacuum residue with 5, 7 and 10% crumb rubber and dividing the amount of added crumb before and after the oxidation process by 2 and 8, 3 and 7 wt.%. As can be seen from the diagram, the oxidation of vacuum residue for 2 h with preliminary mixing with crumb rubber in the amount of 7 and 10 wt.% increases penetration to standard values (83–85)·0.1 mm, however, the softening point of the oxidation products turned out to be low 47–48 °C, which does not meet the requirements of the standard. Separate mixing of vacuum residue and crumb rubber before and after oxidation made it possible to obtain oxidation products with penetration of (77–88)·0.1 mm and an increased softening point of 50–52 °C. It should be noted that the complete process of bitumen production was reduced to 3 h: the oxidation process lasts 2 h, and preliminary and post-oxidation mixing is carried out for 1 h.

Since the values of penetration and softening point of the oxidation product of the vacuum residue with pre-mixing with the addition of 2 wt.% crumb rubber, oxidation for 2 h and subsequent mixing with the addition of 8 wt.% crumb rubber complied with the requirements of the standard, its other technical characteristics were determined to establish the grade of the rubber-bitumen binder. Table 3 shows the physical and mechanical

Table 3
Physical and mechanical characteristics of the rubber-bitumen binder (RBB) obtained by oxidation of vacuum residue modified with crumb rubber

Indicator	Rubber bitumen binder	Requirements of ST RK 2028-2010 for RBB 60/90
Penetration at 25 °C, 0.1 mm	77.0	61-90
Softening point, °C	52.0	not less than 52
Ductility, cm:		
at 25 °C	16.0	at least 12
at 0 °C	6.0	at least 6
Elasticity at 25 °C, °C	60.0	at least 30
Fraas point, °C	-23.0	no higher than -18
Flash point, °C	260.0	not less than 250
Softening point change after aging, °C	4.2	no more than 5

characteristics of the vacuum residue oxidation product with the addition of 2 and 8 wt.% crumb rubber. The penetration of the rubber-bitumen binder is 77·0.1 mm, which satisfies the requirements for the RBB 60/90 grade. The binder has an increased softening point of 52 °C. When crumb rubber is added, ductility usually decreases, which is confirmed by tabular data. The ductility at 25 °C of the binder was 16 cm, at 0 °C – 6 cm. Bituminous binders are characterized by an increased value of elasticity at 25 °C (60 °C) and a low Fraas point (-23 °C). This is very important when operating asphalt concrete pavements in conditions of negative temperatures [23].

The change in the softening point after heating (4.2 °C) characterizes the resistance of bitumen to thermal-oxidative degradation. An important feature of crumb rubber is the presence of antioxidants in its composition, which increases the resistance of bitumen to oxidative degradation [24]. The product of vacuum residue oxidation with the addition of crumb rubber in terms of physical and mechanical parameters corresponds to the rubber-bitumen binder grade RBB 60/90 according to the Standard of the Republic of Kazakhstan (ST RK) 2028-2010.

Based on the obtained rubber-bitumen binder, a hot asphalt concrete was prepared, which contains the following components: crushed stone of the Novo-Alekseevsk quarry (Almaty region, Kazakhstan) from the gravel of a fraction of 5–20 mm – 42 wt.%; shifting fraction 0–5 mm – 47.1 wt.%; activated mineral powder produced by Zhartas LLP (Kordai village, Zhambyl region, Kazakhstan) – 10.9 wt.%; rubber bitumen binder – 5.2 wt.%. The physical and mechanical properties of the asphalt mix were determined by the Standard of the Republic of Kazakhstan 1218-2003 and are

Table 4
Physical and mechanical characteristics of fine-grained dense asphalt concrete mixture prepared based on rubber-bitumen binder

Indicator	Asphalt mix	Regulatory indicators according to ST RK 2028-2010
Water saturation, % by volume	3.5	1.5-4.0
Ultimate compressive strength at 50 °C, MPa	1.9	not less than 1.8
Ultimate compressive strength at 0 °C, MPa	7.1	no more than 13.0
Crack resistance in terms of tensile strength at a split at 0 °C, MPa	4.2	4.0-6.5
Shear resistance according to the coefficient of internal friction	0.85	not less than 0.83
Shear adhesion at 50 °C, MPa	0.49	not less than 0.38
Water-resistance	0.96	not less than 0.9
Water-resistance with long-term water saturation	0.92	not less than 0.8

Table 5
The complex shear modulus of samples at various temperatures

Samples	T = 46 °C	T = 52 °C	T = 58 °C	T = 64 °C	T = 70 °C
			G*, kPa		
Vacuum residue	9.09	4.32	2.21	1.21	0.68
Vacuum residue after aging in RTFO	25.60	11.32	5.15	2.45	1.22
Vacuum residue oxidation product	14.10	5.82	2.52	1.15	0.54
Vacuum residue oxidation product after aging in RTFO	23.60	10.23	4.51	2.05	-
Vacuum residue oxidation product with crumb rubber	15.13	6.93	3.30	1.65	0.86
Vacuum residue oxidation product with crumb rubber after aging in RTFO	17.89	8.29	3.90	1.90	-

presented in Table 4. The test results showed that the prepared asphalt mix meets the requirements of the Standard of the Republic of Kazakhstan 2028-2010 for type B in terms of technical parameters.

An important mechanical property of bitumen is the ability to resist the formation of plastic deformations. The resistance of bitumen to shear strain during multiple loads can be quantitatively expressed by the complex shear modulus G*. Bitumen with a high G* value has high resistance to the formation of plastic strains. Table 5 shows the values of complex shear modulus G* of vacuum residue and its oxidation products before and after short-time aging. In the initial state, the vacuum residue oxidation product with crumb rubber showed the maximum shear modulus compared to the vacuum residue oxidation product without a modifier. As expected, when the temperature rises, the shear modulus of all samples decreases. Short-term aging resulted in an increased shear modulus for all three samples. However, at the same time, its highest values are observed for the vacuum residue itself and its oxidation product.

Figure 7 shows the IR spectra of crumb rubber, vacuum residue and its oxidation products. The products of vacuum residue oxidation at 260 °C for 3 h without and with the addition of 2% crumb rubber with premixing and 8% crumb rubber after oxidation were chosen as samples for analysis. The IR spectrum of crumb rubber is distinguished by a set of absorption bands at 964 and 1062 cm^{-1} with high intensity. The absorption band at 964 cm^{-1} belongs to the vibrations of double C=C bonds of rubber compounds, and the absorption band at 1062 cm^{-1} is due to the presence of sulfoxides formed during the vulcanization of rubber.

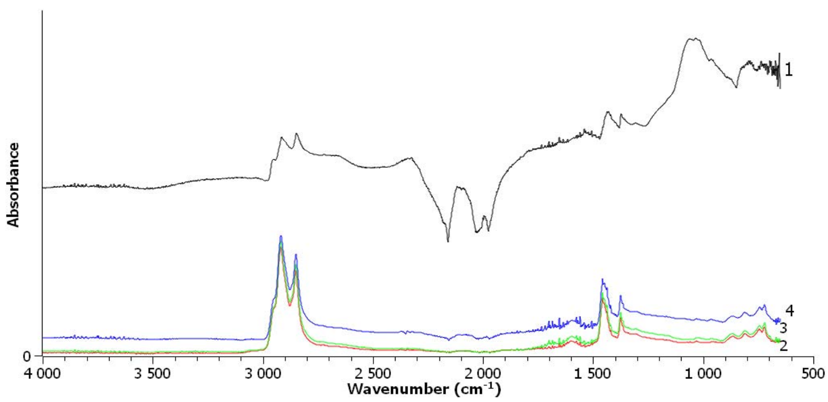

Fig. 7. IR spectra of crumb rubber (1), vacuum residue (2) and its oxidation products without (3) and with the addition of crumb rubber (4).

The spectra of vacuum residue and its oxidation products have the same absorption bands characterizing the presence of aliphatic (absorption bands of C-H bonds in CH_2 and CH_3 groups at 721, 1375, 1457, 2850 and 2919 cm^{-1}) and aromatic structures (absorption bands of H atoms in aromatic rings at 745, 810, 865 and 1616 cm^{-1}). The following functional groups were also found in the composition of vacuum residue and its oxidation products: OH (3629, 3650 and 3676 cm^{-1}); C=O in ethers (1700 cm^{-1}), ketones (1718 cm^{-1}) and aldehydes (1734 cm^{-1}); S=O in sulfoxides (1031 cm^{-1}) and N-H (669 cm^{-1}) in amines.

Table 6 compares the absorption band intensities observed in the IR spectra of the samples. In the sample of the oxidation product with the addition of crumb rubber, the absorption bands are characterized by a relatively high intensity, which indicates an increase in the content of resins and asphaltenes in their composition, which consists of condensed aromatic structures.

Table 6

Intensities of the absorption bands in the IR spectra of crumb rubber, vacuum residue and products of its oxidation without and with the addition of crumb rubber

Wave number, cm^{-1}	Absorption band intensity				Bond and functional group vibrations
	Crumb rubber (CR)	Vacuum residue (VR)	VR oxidation product	Product of oxidation of VR with CR	
659	0.35	-	-	0.08	Deformation vibration of the C=C bond in the cis position
669	-	-	0.06	0.08	Deformation vibration of the N-H bond in amines
721	-	0.1	0.11	0.13	Deformation vibration of the C-H bond in long alkyl chains
745	-	0.09	0.1	0.12	Vibration of four H atoms adjacent to an aromatic ring
810	-	0.08	0.09	0.1	Vibration of two H atoms adjacent to an aromatic ring
865	-	0.07	0.08	0.09	Vibration of the H atom adjacent to the aromatic ring
964	0.33	-	-	0.08	Deformation vibration of the C=C bond in the trans position
1031	-	0.05	0.06	0.08	Stretching vibration of the S=O group
1062	0.4	-	-	-	Stretching vibration of the S=O group
1375	0.24	0.13	0.15	0.16	Deformation vibration of the C-H bond in CH_3 and CH_2 groups
1457	-	0.2	0.22	0.22	
1595	-	0.05	0.07	0.05	Deformation vibration of the C=C bond in the aromatic ring
1616	0.25	0.05	0.06	0.07	
1700	0.24	0.03	0.05	0.07	Stretching vibration of the C=O group in ethers
1718	-	-	0.04	0.05	Stretching vibration of the C=O group in ketones
1734	0.23	0.03	0.04	0.05	Stretching vibration of the C=O group in aldehydes
2850	0.27	0.29	0.32	0.30	Stretching vibration of the C-H bond in the CH_2 group
2919	0.26	0.38	0.39	0.38	
3629	0.1	-	0.02	-	Stretching vibration of the OH group
3650	-.	0.01	0.02	0.01	
3676	-	-	0.02	0.02	

In the IR spectrum of the vacuum residue oxidation product with crumb rubber, absorption bands appear at 659 and 964 cm^{-1}, which are absent in the vacuum residue spectrum. The appearance of these bands, which are characteristic of the IR spectra of rubber, is due to vibrations of double C=C bonds in the cis and transposition, which should be attributed to the rubber being destructured as a result of heat treatment and the resulting rubber substance.

The results of the analysis also confirm the beneficial effect of the modifier on the oxidation process and improve the composition of the resulting product.

4. Conclusion

The effect of crumb rubber size (less than 0.6 mm and 0.6–1.0 mm), its percentage in a mixture with vacuum residue (5–15 wt.%) and the duration of the mixing-oxidation stages on the quality of the resulting rubber-bitumen binders was studied. The analysis has shown that results of the oxidation of vacuum residue modified with crumb rubber have high elasticity and low Fraas point. Results have shown that oxidation and modification of the vacuum residue with crumb rubber lead to an increase in the complex shear modulus. The presented results show the effective impact of crumb rubber on the rate of the oxidation process and the improvement of the physical and mechanical properties of rubber-bitumen binders.

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