

Regulation of the Rheological Properties of Polymer-Bitumen Binders by Ultrasonic Intensification of Mixing Process

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Abstract

The effect of ultrasonic on physico-chemical properties and homogeneity of bituminous material (Western-Siberian and heavy Arlan residue, heavy vacuum gasoil, distillate oil fraction, the shaded fraction) for production of road bitumen by compounding of oxidized product with non-oxidized raw materials is investigated in this article. Evaluation of the colloidal stability of the obtained bitumen was carried out by the research of dynamic viscosity on rotational rheometer, providing the measurement of viscosity at fixed shear rates.

For a sample of bitumen obtained by compounding with ultrasonic machining, the dynamic viscosity with increasing shear rate from 1.5^{-1} s to 30^{-1} s decreased from 178 Pa·s to 100 Pa·s, however, returning to the initial shear rate resulted to restoration of the viscosity until 120 Pa·s, which amounted to 32.2 % from the initial amount. The sample of petroleum road bitumen (PRB) 70/100 obtained by compounding without ultrasonic machining has a higher initial dynamic viscosity (278 Pa·s) but shows the worst resistance to shear loads, which was 58.5 %.

Keywords: polymer-bitumen binder (PBB), ultrasonic, residue, oxidized bitumen

INTRODUCTION

In the XXI century rheology as a science of flow and deformation of materials is gradually becoming the scientific basis of determining the properties of road construction materials and for petroleum bitumen binders (PBB) in the first place [1]. By use of rheological characteristics it is possible not only to evaluate material properties, in particular, bitumen and compositions based on them – toughness, strength, elasticity, plasticity, crack resistance, but also to research the structure formation processes [2]. One of such problems is the study of rheological properties of binders modified with various polymer additives at various technological stages getting for the analysis of possibilities of improvement of their operational properties.

The greatest technological complexity of the production of PBB involves the necessity for effective distribution of

polymer in bitumen base. The distribution of polymer in bitumen binder requires significant energy consumption for long-term (within 6-8 hours) mixture of bitumen base and polymer at high temperatures (160-180 °C). To obtain a homogeneous PBB nowadays it is proposed to use different petroleum plasticizers of oxidized bitumen allowing to dissolve the polymer, and to mix the plasticized polymer and bitumen using expensive and energy-consuming mixing equipment – colloid mills. The use of all these processing methods and also high cost of the polymer greatly increases the cost of PBB production and makes it uncompetitive compared to other bituminous products.

Development of technological way of directed influence on the rheological properties of polymer-bitumen binder will allow to obtain modern road-building binding materials with the most satisfying their exploitation conditions combination of properties.

Ultrasound (US) is used for acceleration and intensification of physical and chemical processes in liquids. The cavitation acoustic currents and other effects occur in the ultrasonic field which contributes to rapid mixing of liquids and solid particles contacting with them. Boundary layers dissolve between different liquids and between liquids and solids, and the processes taking place in these layers are significantly accelerated. Ultrasonic accelerates and improves the degree of homogenization.

Homogenization is a necessary process that ensures a strong homogeneity of the mixture of petroleum feedstocks. The increase in the dispersion of crude oil by ultrasonic experimentally determined by a number of authors [3-7]. The most important criterion for obtaining high quality PBB is its homogeneity. The homogeneity of PBB is influenced by the preparation method of the mixture "based bitumen-polymer".

Based on a review of experience, the aim of this work is to investigate and test under laboratory conditions the intensification of the distribution of polymer in bitumen based with directional influence of ultrasonic machining on the rheological properties of the resulting compositions of polymer-bitumen binder.

Experimental part

It is widely known that PBB is a three-component system: bitumen, plasticizer, polymer. The dispersion medium – bitumen and plasticizer – is of great importance for the quality of PBB. The use of plasticizers allows to modify the hydrocarbon composition and structure of oxidized bitumen in the required direction [8].

We used the following materials to create the PBB dispersion medium:

- petroleum road bitumen (PRB) viscous of grades PRB 60/90 and PRB 90/130 of JSC "Syzran refinery" production;
- industrial oil of grade I-40A according to State Standard (GOST) 20799-88;
- the remains of the vacuum distillation of the West Siberian oil – residues with a nominal viscosity at 80 °C from 50 to 200 s;
- darkened vacuum fraction 450-550 °C (DVF);
- the distillate extract of selective purification of oils(ESPO);

As the PBB dispersed phase we used the Russian thermoplastic elastomer type styrene-butadiene-styrene (SBS) linear structure of grades DST-30-01 of JSC "Voronezhsintezkauchuk" production.

The study of PBB rheological properties of was determined by the indicators of dynamic viscosity at multiple increase shear effects. The value of the dynamic viscosity determines the flow

properties of the binder in the coating during the summer operational period and indicates of the stability of asphalt concrete pavements to rutting and other plastic deformations [9].

Tests were carried out on a rotational rheometer Rheolab QC of "Anton Paar" production, providing measurement of dynamic viscosity at fixed shear rates. To study rheological properties of road bitumen samples used as asphalt bases for PBB preparation, and also PBB samples obtained at the laboratory conditions, we conducted the analysis of physico-mechanical properties, indirectly characterizing the rheology of cementitious materials in terms of: needle penetration depth, melting temperature, the maximum force in extensibility etc. from the list of requirements of State Standard (GOST) 52056-2003 and State Standard (GOST) 33133-2014 included in the Technical regulations of the Customs Union TR TS 014/2011 "Road Safety".

Hydrocarbon group composition was investigated by the method based on the principles of liquid-adsorption chromatography with gradient for displacement of heavy oil fractions boiling above 360 °C. The analysis was carried out in the chromatographic on the installation "Gradient-M" designed by "Institute of Oil Refining" (the Republic of Bashkortostan).

The results of the analysis of physico-chemical properties and PBB group hydrocarbon composition of the plasticizing components are presented in Table 1.

Table 1: Analysis Results of the PBB Plasticizing Components

Indicator	Components - plasticizerspolymer-bitumen binders						
	Tar, sample 1	Tar, sample 2	Tar, sample 3	Tar, sample 4	3BΦ	TГKK	Oil I-40A
Viscosity relative at 80°C, s	32,7	49,8	94,6	201	12,2	3,3	-
Kinematic viscosity at 80 °C, mm ² /s	645,7	954,8	2014	4080	264,4	32,1	14,2
Viscositydynamic at 60 °C, Pa·s	7,1	9,2	12,1	53,6	6,4	-	-
Hydrocarbongroupcomposition, % mass:							
Paraffin-naphthenichydrocarbons, % mass.	23,2	19,9	15,7	10,7	27,7	18,0	70,1
Aromatichydrocarbons, % mass.	48,7	49,2	48,5	48,7	45,8	71,5	29,6
Residues, % mass.	22,7	25,0	28,4	32,1	20,6	10,5	0,3
Asphaltenes, % mass.	5,4	5,9	7,4	8,5	5,9	-	-

As PBB plasticizers it is more appropriate to use heavy oil fractions enriched in benzene hydrocarbons, however, as the techniques of oilplasticizing in PBB production are of wide use, and the dispute about the correct choice of either paraffin-naphthenic or benzeneplasticizer continues to the present time, we conducted our research using two plasticizers: coker gas oil

and oil of I-40A grade.

The results of the analysis of physico-chemical, physico-mechanical properties and hydrocarbon group composition of bitumen used as the basis for PBB preparation are shown in Table 2.

Table 2: Results of Bitumen Analyses Used as the Basis of PBB

Indicator	Samples of Petroleum Road Bitumen			
	PRB 60/90 sample 1	PRB 60/90 sample 2	PRB 90/130 sample 3	PRB 90/130 sample 4
1. Needle penetration depth, at 25 °C, 0,1 mm	89	86	130	128
2. Melting point along the ring and the ball, °C	48	49	44	45
3. Extensibility at 0 °C, cm	4,2	3,8	5,3	5,3
4. Brittleness temperature, ° C	-22	-24	-22	-25
5. Flash temperature, ° C	>290	>290	>270	>270
6. Weight change after deterioration, %	0,2	0,3	0,2	0,1
7. Change of melting temperature after deterioration, °C	7,5	7,3	5,6	6,7
8. Dynamic viscosity, Condition 1 (at 1,5 s-1 and temperature 60 °C), Pa·s	242	214	96	103
9. Dynamic viscosity change due to shearing, Condition 2 (at 1,5 s-1 and temperature 60 °C), %, not more	9,9	8,1	2,2	7,9
10. Dynamic viscosity change after deterioration, Condition 1 (at 1,5 s-1 and temperature 60 °C), Pa·s *	494	495	170	168
11. Dynamic viscosity change due to shearing after deterioration, Condition 2 (at 1,5 s-1 and temperature 60 °C), %, not more	22,3	34,8	7,9	8,2
12. Extensibility at 25 °C, cm	>150	128,2	>150	129,7
13 Maximum tensile force at 25 °C, H	0,706	0,839	0,243	0,305
14. Maximum tensile force at 0 °C, H	96,8	103,3	82,5	81,8
15. Brittleness temperature after deterioration, °C	-22	-23	-21	-24
16 Needle penetration depth, at 0 °C, 0,1 mm:	28	27	33	33
17. Solvability, %	99,6	99,6	99,8	99,7
18. Content of solid paraffins, %	1,3	1,4	1,9	1,7
19. Penetration index	-0,2	-0,1	-0,2	0,0
Hydrocarbon-type content, % mass:				
Paraffin-naphthenic hydro carbons, % mass.	21,3	22,3	21,9	22,9
Benzene hydrocarbons, % mass.	42,0	41,7	44,2	42,2
Gums, % mass.	24,5	24,1	24,7	24,6
Asphaltenes, % mass.	12,1	11,9	9,2	10,3

bitumen binder was prepared by one-step technology by mixing bitumen, plasticizer and polymer. Stirring was carried out in a tank with a Wise Stir HT120DX digital control mixer designed to mix fluids of different viscosities at a given rate. To obtain the required technological effect a waveguide of a special shape was built into the reactor cover, which makes it possible to obtain a developed cavitation zone. An electric signal of high frequency was fed from the generator to a piezoceramic transducer connected to the waveguide. The technical specifications of the ultrasonic unit are given in Table 3.

Table 3: Technical Specifications of the Ultrasonic Unit

Generator Technical Specifications	Value
Power consumption, kW	1,0±0,1
Operating frequency, kHz	20,0±0,1
Efficiency, %	Not less than 93
Power supply, V / Hz	220/ 50
Cooling	Forced air
Flow density, W/cm ²	2,5±0,1

At carrying out the process of preparing polymer modified bitumen in an apparatus with a stirrer, the duration of the mixing process of the components is quite high and depending on the mixer design and the amount of polymer introduced is 6 or more hours. This characteristic has a negative effect on the quality of the final product due to the bitumen deterioration

under the influence of high temperature in the presence of atmospheric oxygen, and it also leads to the formation of coarser dispersed systems. For oxidized bitumen subjected to the most intensive deterioration it is recommended not to raise the temperature of PBB preparation above 160 °C [7]. Due to the fact that ultrasonic machining (USM) leads to an increase in the mixing temperature due to an increase in the intensity of mechanical mixing of liquids [6], USM was started at a temperature of 120 °C for 3-5 minutes with increasing temperature under the influence of ultrasonic to 160 °C. As a reference product we used a laboratory sample of a PBB of identical component composition prepared by mixing the bituminous substrate and the polymer without USM stage. The readiness of the PBB samples was evaluated by homogeneity. Homogeneity is the first sign that allows to classify the resulting mixture as a binder. After achieving homogeneity of the composition, the entire complex of property indices was determined in accordance with the State Standard (GOST) 52056, and changes in the dynamic viscosity of the PBB as a result of the shear action with a multiple increase in the shear rate were determined.

RESULTS AND DISCUSSION

Table 4 shows the results of the investigation of PBB samples based on bitumen of PRB 60/90 and PRB 90/130 grades obtained by a standard agitator and with additional ultrasonic machining of the stirred composition.

Table 4: Results of investigation of PBB samples obtained by mixing bitumen, plasticizer and polymer with a standard agitator and with additional ultrasonic machining of the stirred composition.

Indicator	State Standard (GOST) 52056		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
	PBB 60	PBB 90	PBB 60 without USM	PBB 60 with USM	PBB 60 without USM	PBB 60 with USM	PBB 90 without USM	PBB 90 with USM	PBB 90 without USM	PBB 90 with USM
Sample composition										
PRB 60/90, sample 1, % mass.			88,0	88,0			88,5	86,5		
PRB 60/90, sample 2, % mass.					88,5	88,5			89,0	89,0
Coker gas oil, % mass.			4,5	4,5			4,0	4,0		
Darkened vacuum fraction, % mass.			4,0	4,0	4,0	4,0	4,0	4,0	4,0	4,0
Oil I-40A, % mass.					4,0	4,0			3,5	3,5
DST-30-01, % mass.			3,5	3,5	3,5	3,5	3,5	3,5	3,5	3,5
Results of PBB 60 analysis in accordance with the State Standard (GOST) 52056-2003										
Needle penetration depth, 0,1 mm										

at 25 °C	not less 60	not less 90	98	116	94	112	98	119	94	112
at 0 °C	not less 32	not less 40	28	40	38	46	40	42	38	46
Melting point along the ring and the ball, °C	not lower 54	not lower 51	64	65	64	67	60	62	62	65
Extensibility, cm,										
at 25 °C	not less 25	not less 30	73	97	112	121	93	98	112	121
at 0 °C	not less 11	not less 15	30	41	50	51	45	45	50	51
Brittleness temperature, ° C	not higher -20	not higher -25	-22	-27	-24	-28	-23	-28	-24	-25
Plasticity, %, not less										
at 35 °C	not less 80	not less 85	95	95	96	98	96	95	96	99
at 0 °C	not less 70	not less 75	70	72	71	76	70	78	75	80
Change of melting temperature, °C	not more 5,0	not more 6,0	6,0	4,5	9	5	6,0	4,6	10	5,9
SamplePreparationConditions:										
Temperature, °C			158-160	158-160	158-160	158-160	158-160	158-160	158-160	158-160
Stirringspeed, rpm			900	700	900	700	900	700	900	700
USM, exposure time, min			-	3	-	5	-	3	-	5
Samplemixingtime, h			7,0	5,0	7,0	5,0	6,0	4,5	6,0	4,5

Comparative analysis of Table 4 shows that a short-term (within 3-5 minutes) USM mixture of components: bitumen, plasticizer and polymer allowed to obtain a PBB with higher penetration values at 25 and 0 °C of greater extensibility and plasticity at 25 and 0 °C, and also improve the stability of the binder to thermal and oxidative deterioration, compared to the samples of PBBs obtained by standard intensive mixing at 900 rpm with a paddle stirrer without ultrasonic. The service interval determined by the sum of the melting and brittleness temperature of the samples № 2, 4, 6, 8 which passed the USM is 4-7 °C higher than in the samples of PBB prepared by standard technology.

Simultaneous increase of heat resistance and fracture toughness of PBB samples passing through USM allows us to assume the formation of an elastic structural network in the PBB in the entire volume with a minimum polymer content (3.5% mass.). Elastic structural mesh in PBB, in addition to giving it high elasticity, which fundamentally distinguishes this binder from bitumen, gives it the ability to orientate at negative temperatures. The mechanism of orientation processes is due to the possibility of plastic deformation of this grid at high

viscosity of the system which is able to fix this grid in an oriented, stretched state, thus reinforcing this material [2].

It should be noted that the use of a combination of components (Darkened vacuum fraction and Coker gas oil) for bitumen plasticization makes it possible to obtain PBB 60 and PBB 90 that meet the requirements of the State Standard (GOST) 52056, with no oil in their composition. As it is known [10], the use of PBB in road construction in Russia using the practiced oil plasticization method not only led to unsatisfactory results in the rutting, but also to a deterioration in the resistance to cracking of asphalt concrete. The fundamental index of shear viscosity at a relatively low temperature of 40 °C was often much lower than for base bitumen. The performance of the binder at low temperatures did not reflect satisfactory fracture toughness. The reason for this is the excessive plasticity of the bitumen, plasticized with oils, and the insufficient concentration of the polymer in the plasticized bitumen composition. Binders of this type do not have sufficient resistance to permanent deformation.

If the bitumen is modified by SBS-type polymers, products

with an increased aromatic compounds are recommended for plasticization, since the presence of aromatic blocks in the styrene-butadiene-styrene polymer structure determines its affinity to petroleum bitumen containing a significant amount of aromatic compounds. When using a plasticizer with a high content of aromatic compounds, there is no lubricating finish of the surface of the inert material with oil "sweated" from unstable colloidal formation.

The properties of viscoelastic binders, their characteristics and test methods are described in detail in the scientific papers [11,12]. Standard methods for determination of the bitumen binders rheological properties in the United States are the shear test using a dynamic shear rheometer and a rotational rheometer that allows to determine the change in dynamic viscosity at different levels of shear loads. Therefore, in addition to studies on standard test methods laid down in the list of requirements of State Standard (GOST) 52056, PBB samples were studied to indicate the changes in dynamic viscosity after a multiple increase (from 1.5 sec^{-1} to 30 sec^{-1}) of the shear rate at a temperature of 80°C .

The dependence graphs of the change in the dynamic viscosity of PBB 60 and PBB 90 samples under the influence of US are shown in Figures 1,2.

Comparative analysis of Figures 1,2 shows that the samples obtained with USM at the stage of composition mixing differ by lower values of the initial dynamic viscosities of the PBB, suggesting that the obtained product is more homogeneous. In the samples of PBB № 4 и № 6, which passed the USM, after a multiple increase in the shear rate to 30 sec^{-1} and a further return to the initial rate – 1.5 sec^{-1} , a decrease in the dynamic viscosity change can be observed ($\Delta 2 < \Delta 1$). It is noted that the change in the dynamic viscosity, determined in % of the initial value, in the sample PBB 90, prepared with the coker gas oil plasticization is lower in comparison to the sample PBB 60, prepared with oil. Thus, $\Delta 2$ in sample № 6 - 2.3 % instead of $\Delta 2$ in sample № 4 - 19.8 %

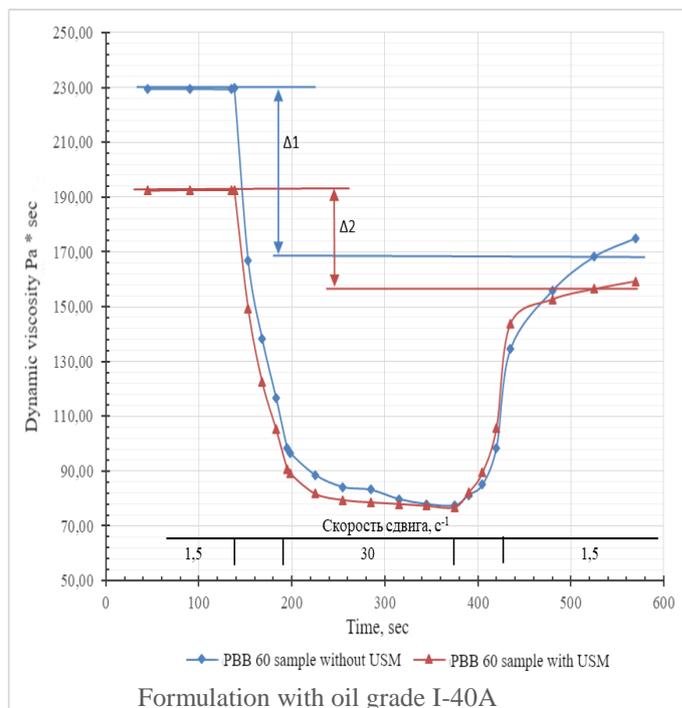


Figure 1: The dynamic viscosity change of PBB 60 samples under the influence of US

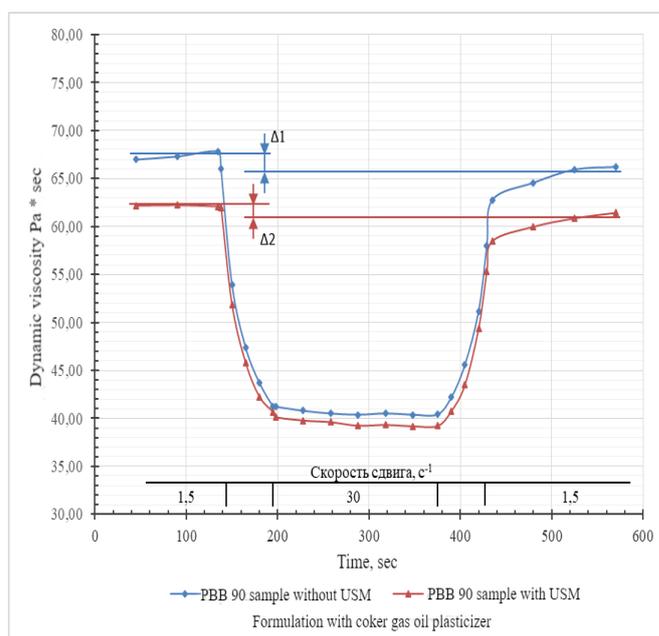


Figure 2: The dynamic viscosity change of PBB 90 samples under the influence of US

CONCLUSION

To sum it up, the data show that the method of PBB preparation by mixing the petroleum bitumen base with a polymer with ultrasonic machining of the mixture in the frequency range of $20.0 \pm 0.1 \text{ kHz}$ for 3-5 minutes allows to improve the rheological properties of the binder and thereby to achieve the required high performance in the asphalt concrete composition.

Research in the direction of the use of coker gas oil as a plasticizer component of PBB is economically feasible. The use of coker gas oil in the production of PBB at the refinery will reduce the amount of coker gas oil in the component composition of the fuel oil, which will lead to a reduction in the content of benzene hydrocarbons in the boiler fuel and thereby improve its environmental characteristics.

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