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Studying Low-Temperature Properties of Bitumen Materials

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Abstract—The effect of polymeric modification with the use of butadiene—styrene thermoplastic elastomer (BSTPE) on the low-temperature properties of BND 90/130 bitumen has been studied on a Fraas instrument and a dynamic shear rheometer. The efficiency of BSTPE modification with respect to the dynamic rheological properties of polymer-modified bitumen (PMB) at negative temperatures has been demonstrated. It has been noted that the complex shear modulus and phase angle of PMB samples are lower than for the bitumen samples and there are no signs of dynamic vitrification.

Keywords: polymer-modified bitumen, low-temperature properties, dynamic shear rheometer, Fraas brittleness temperature, butadiene—styrene thermoplastic elastomer, complex modulus, phase angle

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INTRODUCTION

Bitumen materials find wide application in both road and civil building. In the world and domestic market, there is a broad range of bitumen products: an extensive line of oil bitumens for different spheres of application and protective compositions and tapes, as well as bitumen sealants, mastics, and emulsions for different purposes. The scale of their application imposes a large set of requirements to the properties of bitumen.

For the territory of Russia, where the temperature in the winter period is an average of –18°C [1], it is important to use materials that are resistant to low temperatures. Modification of bitumens by polymers is an efficient solution providing the required properties of bitumen materials. As a consequence, polymer-modified bitumens (PMBs) have become the most intensively developed and studied materials of this field in the last decade [2–4].

In world practice, the leading position as modifiers of bitumen materials is held by thermoplastic elastomers (TPEs)—first of all, butadiene—styrene thermoplastic elastomers (BSTPEs) [2, 5]. According to the data [6], 39% of produced TPEs are used in the world for modification of bitumen and 16% are consumed for mastics and adhesives. At the present time, a great amount of BSTPE grades (with different molecular-mass characteristics, ratios between polystyrene and polybutadiene blocks, etc.) are produced. These parameters determine the key properties of TPEs as a product and, therefore, influence the efficiency of modification.

Bitumen and polymer—bitumen materials are difficult to study due to their multicomponent composition and structural features [2, 4, 5, 7, 8]. In the Russian Federation, the resistance of polymer—bitumen materials to negative temperatures is estimated in compliance with GOST (State Standard) R 52056—2003 by measuring the brittleness temperature by the Fraas method. An increasingly relevant importance is being acquired by the study of PBM properties on the basis of tests under dynamic conditions [9, 10].

Contemporary rheometers provide not only the estimation of their properties, but also efficient prediction of the behavior of materials and a finished product under real conditions of operation [11—13]. In view of this fact, the objective of this study was to investigate the low-temperature properties of PBMs by contemporary methods of testing. For this purpose, a recently developed method for the estimation of low-temperature properties with the use of a dynamic shear rheometer [14, 15] was used.

MATERIALS AND METHODS

In the present study, road bitumen grade BND 90/130 (Kinef company) synthesized by the oil oxidation technique was used. The principal properties of BND 90/130 (GOST 22245—90) are the following:

Property	Value
Needle (0.1 mm) penetration depth (mm) at	
25°C	107
0°C	31
Ring-and-ball softening point, °C	47
Extensibility (cm) at	
25°C	130
0°C	4.5
Fraas brittleness point, °C	–19

Table 1. Recipes of polymer-modified bitumens (content in wt %)

Ingredient	PMB samples				
	B	BM	PMB3	PMB5	PMB7
BND 90/130 bitumen	100	99	96	94	92
I-40A oil	0	1	1	1	1
SBL L 30-01A	0	0	3	5	7

Table 2. PMB properties

Parameter	PMB samples					Testing method
	B	BM	PMB3	PMB5	PMB7	
Needle (0.1 mm) penetration depth at 25°C, mm	107	108	77	57	49	GOST 33136–2014
Extensibility at 25°C, cm	130	85	51.4	42.8	51.9	GOST 11505–75
Softening point, °C	47	48	62	78	92	GOST 11505–73

A linear butadiene–styrene thermoplastic elastomer of SBS L 30-01A grade (Voronezhsyntezkauchuk company) with a bonded styrene content of 30 wt % was selected as a polymer modifier. To facilitate the process of homogenization between the bitumen and thermoplastic elastomer, I-40A industrial oil was added to the bitumen.

In this work, polymer-modified bitumen with different BSTPE concentrations was studied. The recipes of PMBs are given in Table 1.

PMB samples were prepared under laboratory conditions by the following scheme. Bitumen was allowed to stand in a drying chamber for 15 min at a temperature of 160–170°C. Afterwards, thermoplastic elastomer grains and oils were added in specified doses. The resulting mixture was stirred in a colloid mill for 25 min at a rotor-revolution speed of 4000–5000 rpm at 175–185°C. To provide complete homogenization in PMBs, stirring was continued on a blade stirrer (500–600 rpm) for 1 h. At the terminal stage, PMBs were allowed to stand in a drying chamber for 1 h at a temperature of 175–180°C. The characteristics of the prepared PMBs are given in Table 2.

The low-temperature properties of PMBs were studied on a LinteL ATX-20 Fraas automatic system (Neftekhimavtomatika, Russia) and MCR 101 dynamic shear rheometer (Anton Paar, Austria). The preparation of samples for tests on the Fraas system and the dynamic shear rheometer was performed in compliance with GOST (State Standard) 1507–78 and R 58400.9–2019, respectively.

Tests on the dynamic shear rheometer were performed at a temperature of –28, –18, and –8°C. The rheometer, the measuring system of which had a geometry of parallel plates with a diameter of 4 mm and a working gap of 1.75 mm, was used in this work. The rheometer was used in the mode of oscillatory vibrations with controlled deformation $\gamma = 0.1\%$ and a gradual increase in angular frequency (ω = 0.1–250 rad/s). A new sample was prepared for tests at each temperature. The rheological behavior of the bitumen materials was studied by measuring such parameters as complex modulus G^* and its components and phase angle δ in different regimes of shear deformation [12, 13]. The collection and analysis of rheological data were performed with the RheoPlus software, and their processing was carried out by the software provided by the Anton Paar company official representative JSC Avrora in the Russian Federation (Moscow).

RESULTS AND DISCUSSION

The results of measuring the brittleness temperature of samples on the Fraas system are given in Table 3. It can be seen from the presented data that the polymer modifier decreases the brittleness temperature of bitumen materials. After 5–7 wt % of BSTPE were added, the brittleness temperature decreased by 12.5–30%.

Table 3. Results of measuring the Fraas brittleness temperature

Ingredient	PMB samples				
	B	BM	PMB3	PMB5	PMB7
Fraas brittleness temperature, °C	–19	–21	–21	–24	–30

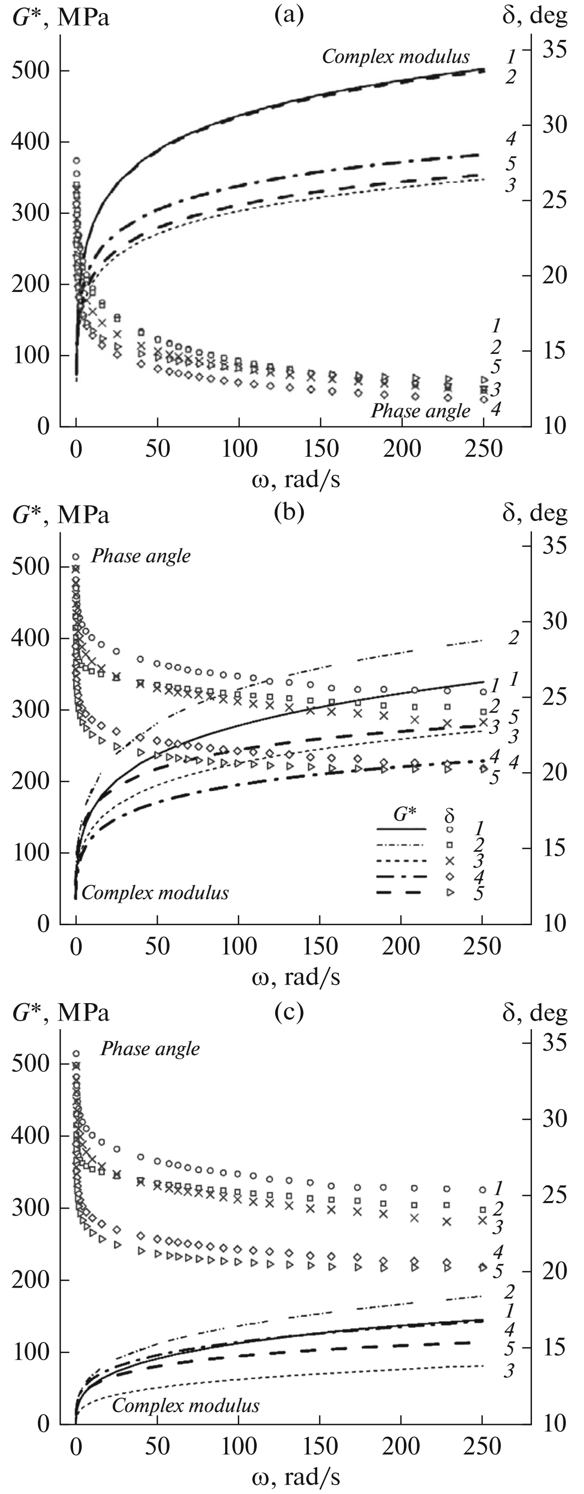

Fig. 1. Complex modulus G^* and phase angle δ vs. frequency ω for PMB samples at a temperature of (a) –28, (b) –18, and (c) –8°C for samples (*1*) B, (*2*) BM, (*3*) PMB3, (*4*) PMB5, and (*5*) PMB7.

The results of testing the samples on the dynamic shear rheometer were used to plot complex modulus G^* and phase angle δ against angular frequency ω at temperatures of –28, –18, and –8°C (Fig. 1).

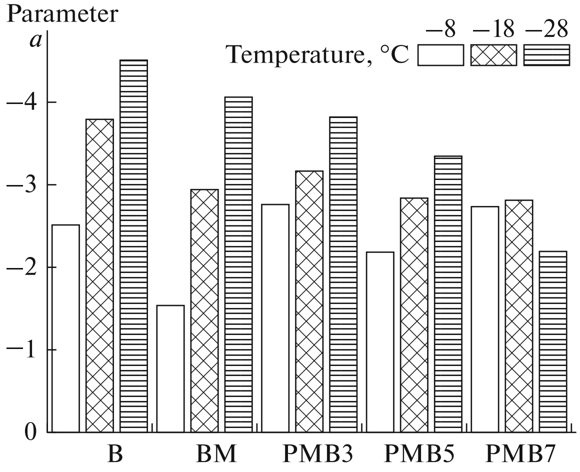

Fig. 2. Effect of testing temperature and BSTPE concentration on parameter *a*.

Complex modulus G^* characterizes the overall resistance of a binder under multiple shear. It is known [12, 13, 16] that, the higher G^*, the less elastic and more rigid a material is and, therefore, the less resistant to destruction under the influence of low temperatures. Curves $G^* = f(\omega)$ of the modified samples are lower than the corresponding curves of bitumen samples throughout the entire range of frequencies and selected temperatures, thus evidencing a lower viscosity and rigidity of PMBs. It should be noted that the polymer modified bitumen with a BSTPE content of 3 wt % demonstrates the best effect on the complex of low-temperature properties, as the ratio $G^*_{\mathrm{BM}}/G^*_{\mathrm{PMB3}}$ is 1.5 at temperatures of –28 and –18°C and 2.1 at –8°C throughout the entire range of frequencies.

Phase angle δ characterizes the viscoelastic properties of a material and quantitatively describe its resistance in the process of shear deformations: the higher δ, the lower its elastic properties and the higher its viscous properties [12, 13, 17]. The phase angle of all the studied samples decreases with an increase in the frequency of tests. The results of estimating parameter a of the linear equation $x = ax + b$ used to describe dependences $\delta = f(\log(\omega))$ are shown in Fig. 2. Parameter a characterizes the slope angle of $\delta = f(\log(\omega))$. It is supposed that, the higher a, the more intense the change in the phase angle with increasing frequency of testing [18] and, as a consequence, the implemented recipe and technological solutions will provide the most optimal combination of viscoelastic properties for bitumen materials in the region of negative temperatures. This effect is most pronounced at a temperature of –28°C for PMB samples with an increase in the thermoplastic-elastomer concentration.

Complex modulus G^* represents a vector sum of accumulation modulus G' and loss modulus G'', which are responsible for elastic (reversible) and viscous (irreversible) deformations [10, 11]. The viscoelastic

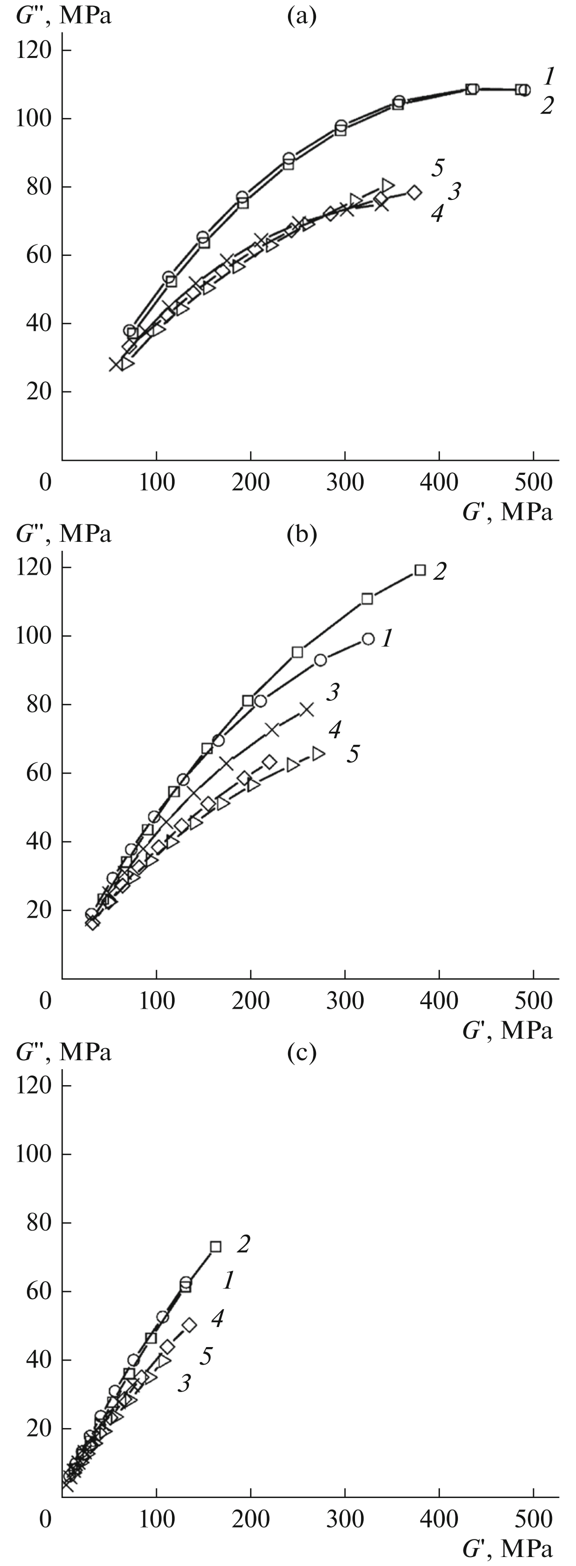

Fig. 3. Loss modulus G'' vs. accumulation modulus G' for PMB samples at a temperature of (a) −28, (b) −18, and (c) −8°C for samples (*1*) B, (*2*) BM, (*3*) PMB3, (*4*) PMB5, and (*5*) PMB7.

properties of a material can also be estimated by plotting the dependence of G'' on G' (Cole–Cole diagrams, Fig. 3) [19, 20].

In the region of low temperatures (−28 and −18°C), the unmodified sample has a characteristic inflection in the curve and a plateau, unlike all the other samples. The maximum in the dependence of G'' on G' can be interpreted as dynamic (mechanical) vitrification occurring under the applied load [15, 20, 21]. The dependence of the loss modulus on the accumulation modulus of polymer modified bitumens has a nearly linear character, and, the higher the BSTPE content, the most pronounced this effect, thus evidencing that there are no dynamic-vitrification signs.

CONCLUSIONS

The results of tests performed by the Fraas method and on a dynamic shear rheometer confirm the advantage of polymer modified bitumen under the conditions of negative temperatures and demonstrate different trends of change in the low-temperature properties of PMBs, such as T_{st} and G^*, depending on the BSTPE content.

Based on the Fraas brittleness temperature values, it has been noted that the low-temperature properties are improved in proportion with an increase in the BSTPE content. The change in the rheological properties of PMBs (G^*, δ, G', G'') depending on the BSTPE concentration has an extreme character. Using the studied materials as an example, it can be seen that PMBs containing no more than 3 wt % of polymer modifier are advisable for application to provide the level of improved low-temperature properties.

However, it is known [22] that bitumen materials essentially change their structure and properties in the processes of their application under the influence of ambient factors, and so it is planned to perform additional studies including the PMB samples subjected to technological and operational aging in the future.

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