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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Thermal Oxidation Resistance of Bitumen Modified with Styrene–Butadiene–Styrene and Ethylene–Vinyl Acetate Copolymers

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Abstract—The effect of a blend of styrene–butadiene–styrene and ethylene–vinyl acetate copolymers on the heat resistance of oxidized bitumen was examined. The structural and rheological properties of the modified bitumen were analyzed.

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An efficient way to control physicomechanical, structural, and rheological properties of oxidized bitumens is to alter their colloidal structure by modification with macromolecular reagents [1–3]. The effects of polymeric additives are different. However, as a rule, if the polymer is compatible with the bitumen, the compound acquires a set of valuable properties of the polymer: elasticity, lower fluidity at elevated temperatures, and crack resistance and flexibility at lowered temperatures. The strength and longevity of asphalt concrete pavements prepared on the basis of polymer–bitumen compounds (PBCs) is largely determined by the resistance of the modified bitumen to thermal oxidative degradation. Elevated temperatures start to strongly affect the PBC structure already in the step of preparing asphalt concrete mix, in the course of mixing heated mineral material with bitumen. The structurization of asphalt concrete is complete in the course of its densification. Each step of the process is accompanied by quantitative changes in structural and rheological properties of bitumen [4, 5]. In the course of operation of an asphalt concrete pavement, the structure and properties of bitumen are subject to the impact of temperature and atmospheric oxygen. Chemical transformations in PBC in the course of thermal oxidation mainly involve two processes: cross-linking and degradation of macromolecules of the dispersed phase. The first process results in formation of three-dimensional polymeric structures, which leads to enhancement of the PBC strength. However, this is accompanied by the loss of elasticity. The compound becomes brittle, and the required service characteristics are lost. The second process, degradation, leads to cleavage of molecular chains and decrease in the molecular weight of the polymer. As a result, PBC loses the mechanical strength [6].

Previous studies [7] showed that styrene–butadiene–styrene (SBS) thermoelastoplastic enhances the strength and viscoelastic characteristics of bitumen and makes it less sensitive to temperature. However, a significant drawback of SBS-modified bitumen is its poor resistance to thermal oxidative degradation. One of possible ways to overcome this drawback, with preservation of all the positive properties of SBS-modified bitumen, is joint introduction into bitumen of styrene–butadiene–styrene and ethylene–vinyl acetate (EVA) copolymers. It is assumed that the polar carbonyl group in EVA macromolecules can interact with bitumen asphaltenes, preventing their coalescence and displacement of the dispersion medium (malthene fraction) associated with them, and thus preventing PBC from becoming more viscous and brittle.

In this study we evaluated the heat resistance of bitumen modified with SBS and ethylene–vinyl acetate copolymers.

Table 1. Change in the softening point and weight loss of PBC after thermal oxidation under static and dynamic conditions

Sample	Softening point before thermal oxidation	Change in softening point after heating, ΔT_s, °C [a]		Weight loss after heating, %	
		static heating test	RTFOT test	static heating test	RTFOT test
Bitumen	48.7	9.1	11.4	0.75	0.93
SBS-modified bitumen	63.5	7.5	8.3	0.45	0.54
SBS-modified bitumen with EVA	75.0	2.7	3.5	0.26	0.38

[a] In accordance with the requirements of the regulations, ΔT_s must not exceed 5°C.

Table 2. Structural and rheological parameters of PBC at 70°C, measured before and after thermal oxidation

Total concentration of SBS and EVA, %	P_{c1}, dPa	P_{c2}, dPa	P_m, dPa	$\chi = P_{c1}/P_m$
1	8714 8714[a]	45000 45000[a]	148330 152509[a]	17.0 17.5[a]
3	10893 11982[a]	75000 77000[a]	174296 172338[a]	16.0 14.3[a]
5	21787 19608[a]	160000 158000[a]	204440 200440[a]	9.2 10.2[a]

[a] Parameters after thermal oxidation.

EXPERIMENTAL

As investigation objects we chose oxidized bitumen of BND 90/130 grade [Novopolotsk Oil Refinery, ring-and-ball softening point 47°C, penetration (0.1 mm units, 25°C) 96], SBS block copolymer containing 31% styrene, and thermoplastic EVA copolymer containing 32–34% vinyl acetate groups. The heat resistance of PBC was evaluated by changes in the softening point and by the weight loss after heating under static conditions in accordance with GOST (State Standard) 22245–90 (300 min at 163°C) and under the dynamic conditions by the RTFOT method in accordance with the requirements of EN 12607-2-TN 13303 (75 min at 163°C in a thin film with air supply), and also by NMR and IR spectroscopy. The NMR spectra were recorded on BS-567A (Czechia, 100 MHz for ^{1}H) and Avance-500 (Germany, 500 MHz for ^{1}H) NMR spectrometers. For recording the ^{1}H NMR spectra we used a 40° radiofrequency pulse. The pulse delay was 5 s. These conditions allowed quantitative analysis of the composition of 30% solutions of PBC in $CDCl_3$. As reference in recording the ^{1}H NMR spectra we used the residual proton signal of the solvent ($CDCl_3$), located at 7.27 ppm. The IR spectra were recorded with a Midac M-200 FTIR spectrometer (USA). The spectra were processed with Grams/32 program (Galactic, USA). Samples were pressed in KBr pellets. The wavenumbers were determined with an accuracy of ±5 cm^{-1}. In interpretation of the absorption spectra we took tabulated data from [8].

The structural and rheological characteristics were determined with a Rheotest-2 rotary viscometer using a cone–plate measuring device. The shear rate was varied in the range 11.1–4860 s^{-1}. Measurements were performed at 70°C, which corresponds to the maximal temperature of operation of an asphalt concrete pavement.

The results of evaluating the heat resistance of the initial bitumen and of bitumens modified with SBS copolymer and a blend of SBS and EVA copolymers (procedures prescribed by GOST 22245–90 and EN 12607-2-TN 13303) are given in Table 1. It can be seen that the softening point of the bitumen sample modified with SBS after thermal oxidation under static conditions decreases by 7.5°C, whereas upon additional introduction of EVA copolymer into the formulation the decrease in the softening point became 2.8 times weaker (2.7°C).

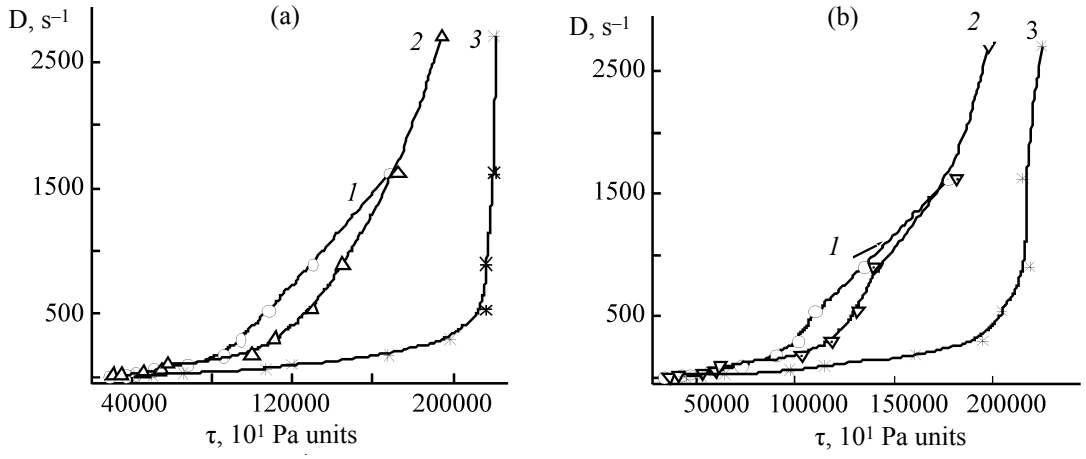

Fig. 1. Flow curves of bitumen modified with SBS and EVA (a) before and (b) after thermal oxidation. (D) Shear rate and (τ) shear strain. SBS + EVA content, %: (*1*) 1, (*2*) 3, and (*3*) 5.

In dynamic tests, ΔT_s decreased from 8.3 to 3.5°C, respectively. Thus, with respect to the change in the softening point after heating, the bitumen modified with an SBS–EVA blend meets the requirements of GOST 22245–90, irrespective of the thermal oxidation conditions. An increase in the heat resistance of the bitumen compound prepared using an SBS–EVA blend, compared to SBS-modified bitumen, is also manifested in a decrease in the weight loss after heating (by a factor of 1.4–1.7 for dynamic and static conditions, respectively).

The resistance to thermal oxidative degradation of the bitumen compound with SBS–EVA copolymer blend can be determined by evaluating structural changes in the PBC colloidal system after thermal oxidation (Table 2, Fig. 1). Analysis of the results of structural and rheological studies of the compounds showed that, after thermal oxidation under static conditions, the structural and rheological parameters determining the cohesion strength P_{c1}, elastoplastic properties P_{c2}, and limiting stress at which the continuity is broken (P_m) for PBC based on the copolymer blend do not change noticeably compared to the nonoxidized samples. It is important that the ratio of the strength limits χ characterizing the strength of structural bonds does not increase. This fact indicates that the size of structural elements of the dispersed phase of the modified bitumen before and after the thermal oxidation is the same. That is, under the conditions of thermal oxidation of PBC, separate chains of the copolymers do not undergo cross-linking which could lead to the loss of elasticity and increase in brittleness.

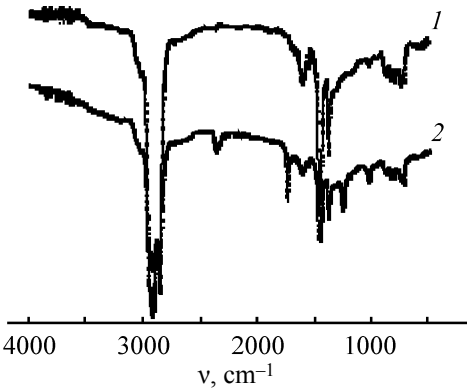

Fig. 2. IR spectra of (*1*) initial bitumen and (*2*) bitumen modified with EVA. (ν) Wavenumber.

NMR spectroscopy is widely used today for studying petroleum systems, being highly informative as applied to such complex systems [9, 10]. The ^{1}H NMR spectra of 30% $CDCl_3$ solutions of PVC based on SBS–EVA blend before and after thermal oxidation are identical, which indicates that the compound has not undergone degradation or any chemical reactions of system components under the conditions of thermal oxidation. The stabilizing effect of SBS–EVA copolymer blend is associated with a specific feature of the chemical structure of EVA, namely, with the presence of a large amount (32–34%) of functional carbonyl groups in its polymeric chain. Analysis of the NMR spectrum of a 30% solution of bitumen modified with SBS and EVA showed that the peak intensity of the signal of the EVA methine proton (δ 4.99 ppm) is lower than the expected value at the given concentration, and the signal is shifted downfield by 0.14 ppm. The shift is due to interaction of

the EVA carbonyl group with bitumen components. The possibility of interaction of carbonyl oxygen atoms with nitrogen-containing cyclic compounds present in bitumen asphaltenes and malthenes is confirmed by the appearance in the IR spectra of PBC prepared with EVA (Fig. 2) of an absorption band at 2360 cm^{-1} corresponding to $N–O^+$ stretching vibrations.

Our studies showed that joint use of EVA and SBS copolymers enhances the bitumen resistance to thermal oxidative degradation. It is important that combination of thermoplastic EVA copolymer with SBS elastomer enhances the adhesion of PBC to the surface of the mineral material and decreases its viscosity at 130°C (minimal temperature of preparation of asphalt concrete mix) to the level characteristics of unmodified bitumen. This makes the asphalt concrete production with this PBC more efficient, as it was shown previously in [11]. Furthermore, additional use of EVA copolymer in bitumen modification allows the SBS concentration to be decreased by a factor of 1.5, with the preservation of the strength and viscoelastic properties of 70°C on the level characteristic of PBC with SBS only. Thus, the use of SBS–EVA copolymer blend allows not only the pavement longevity to be increased owing to enhancement of the resistance to thermal oxidative degradation, but also the power and financial expenditures in PBC production and asphalt concrete paving to be considerably decreased.

CONCLUSIONS

(1) Interaction of the carbonyl group of ethylene–vinyl acetate copolymer with components of bitumen asphaltenes enhances the heat resistance of the polymer–bitumen compound.

(2) The structural and rheological studies confirmed the absence of structural changes in the disperse compound prepared using polymeric additives based on styrene, butadiene, and ethylene–vinyl acetate. Preservation of the strength of structural bonds suggests the identity of the size of structural elements of the dispersed phase of modified bitumen before and after thermal oxidation.

(3) No chemical reactions occur in the disperse system of modified bitumen in the course of thermal oxidation under static conditions.

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