Research on nature of petroleum bitumen interaction with components of complex modifier

P S Belyaev¹, a), V A Frolov¹, L G Varepo², V P Belyaev¹ and E G Bezzateeva ³

¹Tambov State Technical University, 106, Sovetskaya St, Tambov, 392000, Russia
²Omsk State Technical University, 11, Mira ave., Omsk, 644050, Russia
³Moscow Polytechnic University, 38, B. Semenovskya str., Moscow, 107023, Russia

E-mail: bps800@yandex.ru, larisavarepo@yandex.ru

Abstract. The paper deals with petroleum road bitumen interacting with the components of a complex modifier. They are high-pressure polyethylene, thermoelastoplast, polymer packaging waste and surfactants. The analysis of changes are presented in the physical and mechanical properties of binders for road pavements obtained by Fourier-IR spectroscopy, optical methods and standard equipment for measuring the qualitative indicators of road binders based on petroleum bitumen.

Keywords: petroleum bitumen; modifiers; polymers; polymer-bitumen binders; polymer waste; IR spectroscopy; physical and mechanical parameters

1. Introduction

The process of globalization in modern society leads to a significant expansion of the road networks, an increase in traffic flows, traffic loading of freight transport and increasing axial load of vehicles. This brings to a substantial increase in the requirements for the wear resistance of road surfaces, which largely depends on the quality of the binders being used. Numerous studies in the field of road construction and repair indicate the need to modify petroleum road bitumens to improve the efficiency of their use, both in the process of paving, and during further operation [1-3]. In the global practice, the most widely used modifiers of petroleum bitumen are thermoelastoplasts (TEP) of linear and branched structure [4, 5]. The disadvantages of using TEP are their relatively high cost, tendency to delamination of TEP-based polymer-bitumen binders (PBB), and low adhesion to the mineral materials of the asphalt mixture. Therefore, the relevant task is to replace thermoelastoplasts with cheaper blended modifiers using polymer waste, and in particular, waste packaging, with its volume constantly growing and presenting a serious environmental problem for the human race.

2. Problem statement

The purpose of the study is to investigate the nature of interaction with different types of substances for the selected type of petroleum bitumen and to select the composition of the complex modifier, which reduces the cost of the resulting PBB with acceptable physical and mechanical properties. To achieve this, the following tasks should be solved:

- to analyze the structural changes of petroleum bitumens when combined with each of the possible components of a complex modifier;
- to analyze the structural changes of petroleum bitumens when combined with various possible components of a complex modifier;
- to identify physical and chemical interactions between bitumen and modifier components;
- to identify the best option of PBB composition;
– to analyze the possibility of replacing polymers in the modifier with their waste.

3. Objects and research methods
Such materials as high-pressure polyethylene (HPP), thermoplast DST-30-01, polyethylene waste stretch film (WSF), Doros-AP, AMDOR - 9, AMDOR-10, and Adgezol-5 surfactants (SAA) were used as components of complex modifiers for petroleum road bitumen of brand BND 90/130.

The process of modifying road bitumen was conducted at 160 °C in a laboratory mixer over a period of 60 minutes. The interaction of polymer-bitumen binder components was studied using the Fourier spectrometer Infralum FT-801, a stereoscopic microscope MBS-10 and standard equipment for measuring qualitative indicators of petroleum bitumen-based road binders.

To study the directional effect of complex modifiers on bitumen components we first examined the peculiarities of bitumen interaction with each of the components separately, and then searched for mixtures of modifiers, which provide the best quality indicators of the obtained PBB.

4. Results and discussion
Bitumen BND 90/130 is a complex mineral-organic mixture, which consists of various aliphatic and aromatic hydrocarbons [6]. In the IR-spectrum of bitumen (Figure 1) there are stretching (2928 and 2857 cm\(^{-1}\)) and bending (1460 and 1377 cm\(^{-1}\)) vibrations of the C-H bonds in the alkyl groups, as well as bending vibrations of CH\(_2\)-groups in the free paraffin chains (726 cm\(^{-1}\)). Aromatic structures correspond to a band of 1601 cm\(^{-1}\) and peaks in the low-frequency region of 868, 812, and 751 cm\(^{-1}\) [6].

The most common polymer materials used in the field of road bitumen modification are thermoplasts [4, 5].

The peak at 1600 cm\(^{-1}\) characterizes this IR spectrum, and this peak corresponds to the vibrations of the carbon skeleton in the aromatic rings of TEP macromolecules. In this case, the peaks corresponding to the stretching vibrations C (sp\(^2\))-H of the aromatic ring (at 3090-3010 cm\(^{-1}\)) can be identified as part of a broad band in the region of 2700-3100 cm\(^{-1}\). The presence of aromatic rings is also confirmed by overtones in the region of 2000-1640 cm\(^{-1}\), and peaks in the region of 900-675 cm\(^{-1}\). The aliphatic component of TEP is visible in the form of stretching (2923-2830 cm\(^{-1}\), two bands) and bending (1441 cm\(^{-1}\)) vibrations of C-H bonds in -CH\(_2\)-. The absorption bands recorded at 1320 and 976 cm\(^{-1}\) can be attributed to bending vibrations of C-H bonds in unsaturated fragment links of trans-HH=HHH- macromolecules. Vibrations of C=C double bonds explain the peak at 1645 cm\(^{-1}\) [7], which are present in the macromolecules of butadiene-styrene block copolymers.
The IR-spectrum of BND 90/130 bitumen modified with DST 30-01 thermoelastoplast (Figure 2) mainly contains absorption bands, which are typical for the original bitumen and TEP. These are bands corresponding to the stretching vibrations (2,925 and 2,855 cm⁻¹) of alkyl groups, with a slight shift; a band at 1,460 cm⁻¹ which corresponds to the bending vibrations of the \(-\text{CH}_2-\) group; bands at 1,601 cm⁻¹ and peaks in the low-frequency region at 868, 812, and 750 cm⁻¹, which correspond to aromatic structures [6]. At the same time, the band which is typical for the C=C bonds of DST 30-01 at 1645 cm⁻¹ is not detected. This indicates the opening of unsaturated vinyl groups of thermoelastoplast in bitumen forming a rare cross linked polymer inside the BND 90/130 matrix [6]. These changes in the structure of bitumen resulted from its modification by the thermoelastoplast DST 30-01 are manifested in a change in its physical and mechanical properties [8]. With the increase of the thermoelastoplast content combined with bitumen there is an increase of softening point, occurrence and growth of an important indicator of elasticity, but there is a sharp decrease in the depth of needle penetration, with the indicator of this decrease going beyond the requirements of the standards [9, 10].

![Figure 2. IR spectrum of bitumen modified with thermoelastoplast DST 30-01.](image)

To compensate the negative effect of thermoelastoplast on penetration, industrial oils are added to the system, but this aggravates the problem of low adhesion of the obtained PBB to the mineral materials of the asphalt concrete mixture, and also contributes to delamination of the composition [8].

The most common polymer waste is HPP, which makes up a significant proportion of used polymer containers and packaging. The problem of HPP waste recycling is becoming important not only for the environment, but it is also related to the increasing shortage of primary polymer raw materials [13]. One of the ways to dispose of HPP waste is to use it to modify road binders. Figure 3 shows the IR spectrum of high-pressure polyethylene. Commercially available HPP contains both crystalline and amorphous regions (in the spectrum, along with the bands of the amorphous and crystalline regions, there are bands of their mutual influence). HPP molecules have defects due to branching, with ethyl and butyl groups being predominant, unsaturated bonds, end groups, and irregularities in the addition of monomer links.

The study into the kinetics of high-pressure polyethylene melting shows that the complete extinction of solid inclusions is observed in 10...20 minutes after the start of the modification process, depending on the initial size of the granules. Figure 4 shows the IR spectrum of bitumen modified with high-pressure polyethylene.
Figure 3. IR spectrum of high-pressure polyethylene.

It has absorption bands typical for the original bitumen and HPP that correspond to the stretching vibrations (2928 and 2857 cm\(^{-1}\)) and bending (1456 and 1377 cm\(^{-1}\)) vibrations of CH\(_2\)- and CH\(_3\)-groups. The band at 1308 cm\(^{-1}\) is specific for the fan vibrations of the methylene groups of high-pressure polyethylene with a slight shift (1303 cm\(^{-1}\) in the original HPP). The peaks at 1602 cm\(^{-1}\) and in the low-frequency region at 811 cm\(^{-1}\) correspond to aromatic structures \([6, 11-13]\). When adding HPP to BND 90/130, the absorption bands 725 and 751 cm\(^{-1}\) of bitumen join and form a relatively broad 739 cm\(^{-1}\) peak, and the 867 cm\(^{-1}\) peak shifts to the 884 cm\(^{-1}\) region. Along with a distinct absorption band at 613 cm\(^{-1}\), this may be due to the formation of a supermolecular structure in the PBB.

Figure 4. IR spectrum of bitumen modified by HPP.

These changes in the structure of bitumen due to high-pressure polyethylene modification are manifested in changes in its physical and mechanical parameters \([8]\). With the increase in HPP content mixed with petroleum bitumen, a lower intensity of softening point increase is observed compared to thermoelastoplast modification, less pronounced decrease of needle penetration depth, and insufficient level of elasticity \([8-10]\). This confirms the conclusions made by other experts about the lack of polyolefins effectiveness for bitumen modification \([14-16]\).
To increase the adhesion degree of bitumen with mineral materials of asphalt concrete mixtures (crushed stone, granite, sand) surface-active adhesive additives (SAAA) are added to the binder. The effect of the four types of SAAA presented above on the physical and mechanical properties of bitumen was studied. The processes of combining SAAA with BND 90/130 bitumen were performed at the same temperature and mixing time. The study shows that the introduction of adhesive additives in bitumen does not form in the modified bitumen such an important indicator as elasticity, but has a significant impact on the penetration and ductility of the binder. It is found that Amdor-10 additive is the most suitable for combined use with thermoplast and thermoelastoplast when modifying bitumen [17].

Figure 5 shows the IR spectrum of bitumen modified with the surface-active adhesive additive Amdor-10. When using Amdor-10 we observe the absence of the 3180 cm\(^{-1}\) band and the development of a weakly intense 3310 cm\(^{-1}\) band (stretching vibrations of hydroxyl OH groups), indicating the presence and rearrangement of hydrogen bonds.

Further studies were performed using various mixed compositions based on HPP, thermoelastoplast DST-30-01, and waste polyethylene and SAAA stretch film. The possibility of partial replacement of DST-30-01 thermoelastoplast with polyethylene or its waste products in the form of OSB in order to reduce the cost of the resulting PBB was investigated. However, in the absence of SAA, the combined use of thermoelastoplast DST-30-01 and polyethylene, both primary and waste does not provide comparable parameters of the modified bitumen BND 90/130 (Table 1) relative to pure thermoelastoplast modification [8].

**Table 1.** Changes in the physical and mechanical parameters of road binder resulting from the content of polyethylene and thermoelastoplast

| Indicator                          | Content of thermoelastoplast / thermoplast, Mass, % |
|------------------------------------|----------------------------------------------------|
| Depth of needle penetration at 25 °C, × 10 mm | 1.0 2.0 3.0 1.0 2.0 3.0 1.0 2.0 3.0 |
| Ductility at 25 °C, mm              | 375 480 640 415 640 715 520 670 725 |
| Softening point, °C                | 57 59 68 63 68 75 72 75 79 |
| Elasticity, %                      | 55 58 66 60 65 72 63 66 73 |
In addition, the adhesion of the obtained composite binders to the fillers of asphalt mixtures does not meet modern requirements. Therefore, further research was aimed at studying the nature of changes in the physical and mechanical characteristics of bitumen with the additional use of adhesive additives.

Figure 6 shows the IR spectrum of BND 90/130 bitumen modified with a complex modifier based on DST-30-01 thermoelastoplast, HPP thermoplast, and adhesive additive Amdor-10.

In general, the spectrum has HPP and TEP absorption bands specific for the original bitumen corresponding to the stretching vibrations (2924 and 2854 cm\(^{-1}\)) of alkyl groups, with a slight shift; the bending (1460 and 1377 cm\(^{-1}\)) vibrations of the CH\(_2\) - and CH\(_3\) - groups.

The band is observed at 1308 cm\(^{-1}\) and it is typical for the fan vibrations of the HPP methylene groups with a slight shift (1303 cm\(^{-1}\) in the original HPP). The peaks at 1600 cm\(^{-1}\) and in the low-frequency region at 814 cm\(^{-1}\) correspond to aromatic structures [6, 11-13]. With the combined use of HPP and TEP for the modification of BND 90/130 with Amdor-10, the band specific for the C = C bonds of DST 30-01 at 1645 cm\(^{-1}\) is not detected, which is obvious for the interaction of bitumen with thermoelastoplast. This interaction leads to the formation of a rare cross linked polymer inside the BND 90/130 matrix [6]. The use of surface-active adhesive additive Amdor-10 reduces the surface tension at the component interfaces. In this case, along with a rare cross linked network of thermoelastoplast in bitumen, an additional network of linear high-pressure polyethylene molecules forms. These molecules are bound to the thermoelastoplast and bitumen by the Van der Waals forces.

Figure 6. IR spectrum of bitumen modified with a mixture of HPP, thermoelastoplast DST 30-01 and Amdor-10.

In this case, the absorption bands 725 and 751 cm\(^{-1}\) of bitumen join and form a relatively wide peak of 742 cm\(^{-1}\), and the peak of 867 cm\(^{-1}\) shifts to the region of 877 cm\(^{-1}\). In addition, a well-defined absorption band certain for the interaction of bitumen with HPP appears at 611 cm\(^{-1}\). This band may be caused by the formation of a supermolecular structure in PBB.

Figure 7 shows a photo of bitumen modified with a complex modifier based on thermoelastoplast DST-30-01, thermoplast HPP, and adhesive additive Amdor-10. Regular rounded inclusions of products in the interaction of light bitumen fractions with molten HPP droplets are observed. For the used concentration (1 - 3 wt %), a substantial proportion of the HPP can be dissolved in the low-molecular-weight part of the bitumen [18, 19]. The thermoplastic macromolecules form an additional spatial network through meshing and intertwining of chains, as well as due to the Van der Waals interactions between macromolecules of the modifier and bitumen components. The dark color is due to inclusions of asphalt-resinous deposits of bitumen, which are not solvents for thermoplast. HPP due
to its properties, along with thermoelastoplast, provides elasticity to the modified bitumen and additional strength, acting as a reinforcing element.

Figure 7. Photo of a sample of bitumen modified by the joint use of DST-30-01, HPP and Amdor-10.

These changes explain the improvement of the qualitative indicators of the resulting BPS compared to the original bitumen. The improvements include a significant increase in the softening point and the acquisition of such an important indicator of PBB as elasticity (Table 2).

Table 2. Changes in the indicators of road binder depending on the content of HPP and TEP in the presence of Amdor-10.

| Indicator                        | Content of thermoe lastoplast / thermoplast, mass.% |
|----------------------------------|---------------------------------------------------|
|                                  | 1.0 | 2.0 | 3.0 | 1.0 | 2.0 | 3.0 | 1.0 | 2.0 | 3.0 |
| Depth of needle penetration at 25°C, × 10 mm | 73  | 65  | 57  | 70  | 62  | 53  | 67  | 58  | 50  |
| Ductility at 25 °C, mm           | 189 | 508 | 680 | 339 | 625 | 751 | 442 | 676 | 768 |
| Softening point, °C              | 63  | 66  | 68  | 67  | 71  | 74  | 73  | 77  | 81  |
| Elasticity, %                    | 48  | 75  | 83  | 54  | 78  | 85  | 60  | 83  | 88  |

Studies show that a partial replacement of thermoelastoplast DST 30-01 by polyethylene OSB waste in the presence of the adhesive additive of brand Amdor-10 enables to achieve comparable results of changing physical and mechanical properties of road bitumen similar to the case of using the primary HPP (Table 3).

Table 3. Changes in the indicators of road binder depending on the content of OSB and TEP in the presence of Amdor-10.

| Indicator                        | Content of thermoe lastoplast / thermoplast, OSB, mass.% |
|----------------------------------|--------------------------------------------------------|
|                                  | 1.0/1.0 | 3.0/1.0 | 2.0/2.0 | 1.0/3.0 | 3.0/3.0 |
| Depth of needle penetration at 25°C, × 10 mm | 71  | 55  | 61  | 65  | 65  | 51  |
| Ductility at 25 °C, mm           | 220 | 648 | 612 | 408 | 716 |
| Softening point, °C              | 61  | 66  | 68  | 71  | 79  |
| Elasticity, %                    | 49  | 83  | 76  | 64  | 84  |

This opens up prospects for further reducing the cost of the resulting polymer-bitumen binder using waste. In addition, large-scale production of PBB based on polyethylene waste allows for the
secondary use of significant volumes of contaminated waste from polymer containers and packaging made of this thermoplas.

5. Summary and conclusion
This paper presents the results on the interaction of petroleum road bitumen with the components of a complex modifier and their various combinations. The analysis is performed using the method of Fourier-transform IR spectroscopy, optical methods and standard equipment for measuring the qualitative indicators of petroleum bitumen-based road binders. It is revealed that the adhesive additive AMDOR-10 along with the rare cross linked network of thermoelastoplast in bitumen form an additional network of macromolecules of high pressure polyethylene due to meshing and intertwining of chains, as well as due to the Van der Waals interactions between macromolecules of the modifier and bitumen components. This allows for a partial replacement of thermoelastoplast DST 30-01 in the complex modifier of petroleum bitumen BND 90/130 with high-pressure polyethylene. Comparable results are also obtained when thermoelastoplast is partially replaced by polyethylene waste, which opens up the prospects of using long-degradable thermoplastic waste in road construction.

6. References
[1] Zhu J, Balieu R and Wang H 2019 The use of solubility parameters and free energy theory for phase behaviour of polymer-modified bitumen: a review Road Materials and Pavement Design pp 1–22
[2] Sienkiewicz M, Borzędowska-Labuda K, Wojtkiewicz A and Janik H 2017 Development of methods improving storage stability of bitumen modified with ground tire rubber: A review Fuel Processing Technology 159 pp 272–279
[3] Polymer modified bitumen: Properties and characterization 2011 Edited by Tony McNally. Oxford: Woodhead Publishing 404 p
[4] Kaya D, Topal A, Gupta J and McNally T 2019 Relationship between processing parameters and aging with the rheological behaviour of SBS modified bitumen Construction and Building Materials 221 pp 345–350
[5] Kaya D, Topal A, Gupta J and McNally T 2020 Aging effects on the composition and thermal properties of styrene-butadiene-styrene (SBS) modified bitumen Construction and Building Materials 235 pp 117450
[6] Makarov D B, Agund E M, Ayupov D A, Murafa A V, Faskhutdinov K A, Khozin V G and Yakhin R G 2015 Study of bituminous-polymer binders modified with mixed thermoplastics by IR spectroscopy Izvestiya KGASU 34(4) pp 280–286
[7] Tarasevich B N 2012 IR spectra of the main classes of organic compounds. Reference materials (Moscow: Lomonosov Moscow State University) 55 p [in Russian]
[8] Belyaev P S, Mishchenko S V, Belyaev VP and Frolov VA 2017 Monitoring of the changes in the characteristics of petroleum bitumen in its interaction with the polymer AIP Conference Proceedings 1876(1) 020096
[9] GOST R 52056-2003 Polymer-bitumen road binders based on styrene-butadiene-styrene block copolymers. Technical conditions. URL: http://docs.cntd.ru/document/1200032030 (accessed 31.10.2020)
[10] GOST EN 13398-2013 Modified bitumen and bituminous binders. Definition of elasticity. http://docs.cntd.ru/document/1200108308 (accessed 31.10.2020)
[11] Peintner P, Coleman M and Koenig J 1986 Theory of vibrational spectroscopy. Appendix to polymer materials (trans. engl. Moscow: Mir) 580 p
[12] Kuptsov A Kh and Zhizhin G N 2013 Fourier-Raman and Fourier-IR spectra of polymers [Electronic resource] (Moscow: Technosphere) 696 p. - Access mode: http://www.iprbookshop.ru/31880. - EBS “IPRbooks”. Accessed 03.11.2020)
[13] Gordeeva I V, Melnikov D A, Gorbatova V N, Reznichenko D S and Naumova Yu 2020 A Study of modification process effect on the group composition of bitumen and modifiers by Fourier-IR-spectroscopy *Fine Chemical Technologies* **15** (2) pp 56–66

[14] Zhu J, Birgisson B and Kringos N 2014 *European Polymer J*. **54** pp 18–38

[15] Polacco G, Berrincioni S, Biondi D, Stastna J and Zanzotto L 2005 *European Polymer J*. **41** (12) pp 2831–2844

[16] Yeh P H, Nien Y H, Chen J H, Chen W C and Chen J S 2005 *Polymer Eng. &Sci.* **45** (8) pp 1152–1158

[17] Frolov V A, Belyaev V P, Malin P, Belyaev P S and Sokolov M V 2020 Research on the prospects of recycling waste polymeric packaging in the processes of modification of petroleum bitumen // Bulletin of Tula State University: Automation: problems, ideas, solutions: Proceedings of the national correspondence scientific and technical conference "APIR-25" (Tula: Publishing House of Tula State University) 179–183

[18] Galdina V D 2009 Modified bitumen. (Omsk: SibADI) 228 p

[19] Wolfson I S et al. 2016 Modification of bitumens as a way to increase their operational properties *Bulletin of Technological University* **19**(17) pp 29–33