Modern modifiers for obtaining polymer-bitumen binders

A Khaibullina¹, B Vagapov¹, I Galimullin¹, I Mukhamatdinov²

¹Kazan National Research Technological University, Kazan, Russia
²Kazan Federal University, Kazan, Russia

E-mail: iimuhamatdinov@gmail.com

Abstract. Currently, studying additives to petroleum road bitumen for improving their quality generates a growing interest in research field. Actually, this is related to the requirements for polymer-bitumen materials which are constantly becoming tougher, and therefore the need to develop and produce new polymer-bitumen binders. In this paper we considered the most frequently used effective additives and analyzed their positive and negative sides.

1. Introduction

At present, roads are one of the most important means of communication for the entire population in our country. The number of cars is increasing every day, and therefore road surface loading is increasing. For example, the growth in car turnover is expected to increase by 8.5% in 2019, compared with 2018 [1]. At the same time, the quality of compliant roads is 50%, which means that only half can withstand the load and last for 12 years (according to the Government Decree No.539 of August 23, 2007). Currently, there is a project “Safe and high-quality roads” approved by the Presidium of the Presidential Council for Strategic Development and Priority Projects, which is valid until 2025, in order to bring the road to a normal transport and operational condition. It aims to increase the number of quality roads up to 85%. To achieve these goals, an integrated approach to the design of technologies for the production and laying of asphalt concrete pavements is needed. One of the key components that is responsible for the quality of roads is polymer-bitumen binder (PBB). It enables the formation of a strong, stable structure of asphalt concrete, which makes it possible to withstand unsatisfactory weather conditions, as well as to improve the plastic properties. In order to obtain a suitable PBB, measures are being taken to use certain components in its composition, as well as factors affecting the properties.

One of the current problems concerning bitumen binders is the transition to the requirements of new regulatory documents [2]. The first GOST (state standard) for quality control of bitumen was GOST 22245-90 "Viscous road bitumen". However, GOST 33133-2014 "Bitumen oil viscous road" was introduced to replace it. It should be noted that GOST 33133-2014 was adopted only in 2014. Over the period of 24 years, the number of loads on the road surface has increased significantly which led to the formation of gauge and a large number of cracks as a result of non withstanding them. By the time of GOST 33133-2014 introduction, not all the production of bitumen materials could be adjusted to meet the product requirements and continued to produce bitumen materials according to the old standards.
As for the PBB, the existing GOST from 2003 does not respond to modern calls for binding materials. This led to the development in 2016 of preliminary national standards PNST 82 and PNST 85 on the basis of foreign regulatory documents. The PNST data contains technical requirements for the physico-chemical quality indicators of bitumen binders (BB), which are divided into PG marks by the upper and lower values of operating temperatures in the aggregate, respectively, denoted by X and Y, for example, PG 40-28. Each brand is associated with indicators that allow to normalize BB. However, in PNST 85-2016, many of them do not provide an accurate picture of the properties of BB. For example, the mass of the bitumen binder after aging is measured, in addition to measuring the temperatures at which the experiment is carried out to determine the low-temperature stability. Regulatory documents should be directed to the production of quality products, the control of which is carried out through the rheological properties of PBB (flash point, dynamic viscosity). However, these indicators in the PNST do not have clear boundaries that can formulate a quick and correct conclusion regarding the properties of the PBB. The advantages of this regulatory document are the involvement of the load on the roadway and the average speed of vehicles when assessing the properties of a polymer-bitumen binder.

In order to improve the quality of bitumen, corresponding to the new regulatory documents, modification of bitumen is envisaged to obtain bitumen binders, the quality indicators of which reach the maximum possible values. There are several ways to carry out this process, the most popular of which is the addition of a modifier to the bitumen environment, most often the polymer — a highly elastic material [3], thereby obtaining a polymer modified bitumen (PmB). This component in most cases leads to a decrease in brittleness temperature, an increase in elasticity and an improvement in performance properties, which increase the durability of road surfaces and provide greater resistance to tiling and destruction.

Researchers are very interested in using modifiers. Experiments are being conducted to identify the best modifying substance, additives, their ratio in BB, which could reveal the best version of a quality product. However, there are difficulties in research, which is manifested in the poor compatibility of bitumen and modifier. The particles of the modifier are not completely dissolved in the bitumen medium, thereby violating the uniformity of the bituminous material.

2. Popular modifiers for Polymer-Bitumen Binders

2.1 Styrene-butadiene-styrene (SBS) modifiers

In connection with the constant tightening of requirements for bitumen-based products, an urgent task for research is to study the properties of various modifiers, which can significantly improve the performance properties of these materials. One of the most popular and common modifiers is styrene-butadiene copolymer — styrene-butadiene-styrene (SBS).

Modifying bitumen by SBS polymer leads to a significant improvement in rheological properties, which was investigated in [4-14]. In their study [4], Slowik et al investigated Venezuelan (V) and Russian (R) bitumens with SBS content ranging from 0-9%. Rheological properties in a wide range of temperatures (consistent with the actual conditions of operation of pavements) were studied on a dynamic shear rheometer (DSR).

According to their results, we can conclude:

- at high temperatures the shear modulus \(|G^*|\) increases, which leads to increased stability with constant deformation;
- at low temperatures, the shear modulus $|G^*|$ decreases, which contributes to increased resistance to thermal cracks.

Also, an analysis of the shear modulus index (SMI) values showed a significant effect of the SBS copolymer content on reducing the sensitivity of asphalt binders to changes in their rigidity at various temperatures. Reducing the temperature susceptibility of the modified bitumen should be considered as one of the most important advantages of using SBS copolymer as a bitumen modifier.

However, styrene-butadiene-styrene has several disadvantages. Firstly, it is characterized by poor solubility in bitumen, as a result of which it becomes difficult to obtain a homogeneous mixture, and, secondly, it has a high cost due to the small number of manufacturers. In Russia, the only manufacturer of SBS is Voronezhsintezkauchuk OJSC (part of SIBUR Holding PJSC).

At present, the combination of SBS with other components that provide its good solubility in the bitumen medium and allow to improve the performance properties is being actively studied. For example, in [15] SBS was studied in combination with stearic acid, epoxy resin, tall oil and polyethylene polyamine (PEPA), which in turn give bitumen a number of properties described in Table 1.

| Component                        | Bitumen properties                                                                 | Content       |
|----------------------------------|-------------------------------------------------------------------------------------|---------------|
| Styrene-butadiene-styrene DST-30-01 | - improves the performance properties of PBB: elasticity, crack resistance, resistance to rutting | 4-8 %         |
| Stearic acid                     | - act as plasticizing components that accelerate the process of dissolution and homogenization of SBS in the mass of bitumen; | 2-4 %         |
| Tall oil                         | - improve adhesion, namely adhesion, of bitumen to stone materials                  | 6-8 %         |
| Epoxy resin                      | - helps to increase the softening temperature, reduce the brittleness temperature, which will contribute to an increase in the crack resistance and shear resistance of asphalt concrete pavements | 1-3 %         |
| Polyethylenepolyamine            | in the amount of 1% by weight of epoxy resin                                        |               |

It should be noted that the properties of bitumen are improved when using the above components in the amount given in table. 1. However, an increase in styrene-butadiene-styrene content (grade DST-30-01) leads to the need for additional injection of tall oil (more than 8%) to completely dissolve the polymer in the bitumen, which contributes to a decrease in tensile properties, plasticity interval and an increase in brittleness of the prepared PBB.

2.2. Sulfur containing modifiers

Creating a modified bitumen with the best performance properties covers a wide range of additives, the most interesting of which is the use of sulfur [16-18]. This is due to the fact that standards for reducing the sulfur content in petroleum products are being actively introduced. For example, the International Maritime Organization of the United Nations (IMO) requires reducing the sulfur content...
in marine fuel from the current 3.5% to 0.5% by 2020. Consequently, the amount of free sulfur becomes greater, which makes it possible to involve it in the production of modified bitumen. The study of [16] reveals the properties of sulfur, where VG-30 is used as the source of bitumen, which is commonly used for most Indian roads. Based on their experiments, it can be concluded that sulfur, being in a medium of bitumen, contributes to the formation of three-dimensional structures that enhance the bitumen and thereby reduce the thickness of the road surface. Moreover, the addition of sulfur in the amount of 2% and 3% increases the viscosity of the bituminous binder, as a result of the restructuring of the internal molecular structure of sulfur in the bitumen matrix, increases the resistance to rutting, cracking and aging. However, the maximum permissible heating temperature of sulfur-bitumen binders, at which all binders, regardless of the sulfur content, have practically the minimum and the same viscosity, is 140 °C. Further heating is unacceptable, since at a temperature of about 150 °C begins the release of toxic gas - hydrogen sulfide, formed as a result of exposure to sulfur dioxide with the products of the dehydrogenation of bitumen components which presents the weak side of the modification of bitumen.

In addition to elemental sulfur, various sulfur-containing compounds are used, for example, dodecylbenzene sulfonic acid (DBSA) [17]. The presence of strong sulfonic acid (SO$_3$H) in the composition of this modifier ensures effective interaction of surfactants with asphaltenes. At the molecular level, modification occurs through the protonation of heteroatomic asphaltene by the components of the sulfonic acid group of the DBSA. This process leads to the formation of asphaltene/DBSA ion pairs with strong bonding interactions, capable of stimulating further electrostatic interactions with other ion pairs. Since the amount of DBSA used on the number of active constituents in the asphaltenes molecules was not high enough to ensure complete coverage or micelle formation of individual aggregates, the DBSA acted to promote the association of the asphaltenes molecules. On this basis, the addition of this additive to the selected bitumen in concentrations of up to 3% by weight, significantly improves its viscous flow characteristics at 60 °C and the viscoelastic response in the temperature range from 30 to 110 °C. In addition, the magnitude of the improvement increased with increasing concentration of the additive and was practically independent of the treatment temperature. Accordingly, the modified binder DBSA has improved thermomechanical properties compared to its original bitumen, which on a wider scale gives large effective volumes of the asphaltene fraction, which improve the rheological and thermal properties of bitumen.

2.3. Nanomodifiers

In the modern world, nanotechnologies have taken one of the leading positions in the development of our society, as well as becoming widespread in the production of bitumen binders. There are many varieties of these additives, the most common are nanotubes [19-21]. Their representatives are multilayer carbon nanotubes (MCNTs) and single-layer carbon nanotubes (SCNTs), which, due to good dispersibility in the bitumen matrix, are difficult to distinguish. Mainly, this additive allows to increase the elasticity.

In addition, inorganic nanoceramic powder (NCP) [22], obtained from ceramic waste, can also be added to the bitumen composition. With an increase in the content of this modifier, the viscosity and area of heteroatoms in bitumen increase, due to the influence of NCP in the restructuring of molecules, which allows to obtain a new polyaromatic system. The change in the physicochemical and rheological properties of bitumen is presented in Table 2.
Table 2. Changes in the physico-chemical and rheological properties of bitumen modified by NCP.

| NCP content | Penetration | Softening temperature | Viscoelasticity |
|-------------|-------------|------------------------|-----------------|
| 2 %         | Increased by 11% | Increased from 2 to 4 °C with growth from 2 to 6% | - |
| 4 %         | Increased by 15.2% | - | - |
| 6 %         | Increased by 20.6% | - | At a temperature of 46 °C, the angle [G/sin (d)] is 22.26 (for base bitumen 60/70 14.62) |

As can be seen from the table 2, the properties of base bitumen 60/70 with the addition of nanoceramic powder increase, indicating an improvement in the quality of bitumen.

Another interesting direction is the study of multidimensional nanomaterials. For example, in [6], the materials used contained 1% organic expanded vermiculite, 2% nano-silica (SiO2), 2% nano-titanium oxide (TiO2), 2% zinc-nanoxide (ZnO). The effect of inorganic nanoparticles, which limit the movement of asphalt molecules, makes it possible to achieve high stability of bitumen at high temperatures. In turn, exfoliated vermiculite, spreading throughout the asphalt matrix, improves the deformation resistance of asphalt.

Nanomaterials used as additives to bitumen are diverse. In addition to the synthetic components, they can also contain natural ones. One of such inclusions may be nanoclay-natural montmorillonite clay [12; 23-28], which, to facilitate its dispersion in bitumen, is organically modified by replacing metal cations with quaternary ammonium cations (N, N-dimethyl-dihydrogenated) at a concentration of 92.6 meq/100g of clay. Particles of nanoclay in the composition of the modifier, being very close to each other, limit the movement of polymer molecules, and thereby minimize their coalescence. While thin polymer droplets act as a connecting point between particles. It can be noted that the inclusion of nanoparticles in the PmB, the interfacial voltage between the polymer and bitumen decreased, and the dispersion of the polymer in the bitumen matrix improved.

Another interesting addition of this block of representatives is nano-sized coconut charcoal [29], whose particle size is 1-100 nm. These nano-sized particles are well dispersed in the environment of bitumen, and also create a strong bond with it. This in turn increases the resistance of bitumen to the formation of cracks at high temperatures and leads to an increase in viscosity at 135 °C. However, it can be noted that large-sized particles of coal, forming a high bitumen viscosity, are poorly dispersed in bitumen. Nanotechnologies are currently discovering new varieties of nanoscale particles that can be used in the production of PmBs, helping to obtain the best indicators of the properties of bituminous binders.

3. Conclusion

Despite the constantly tightening requirements for polymer-bitumen binders, a large variety of materials-modifiers allows you to get modern high-quality PBB. In addition to the development of bitumen additives, various combinations of already existing modifiers are also being actively investigated. In this paper, modern modifiers for bitumen materials were considered, among which SBS, sulfur, and nanomaterials are most often in studies. However, none of them is not without flaws, which in the future may outweigh their positive qualities. In this regard, there is a large number of works aimed at developing new formulations and technologies for producing modern polymer-bitumen materials.
Acknowledgments
The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

References
[1] Orlov D V 2018 Inter-sectoral conference "RRO BITUM AND PBV" as a tool for the development of the industry (in Russian)
[2] Korotkov A 2018 Unification of requirements for binding and ensuring the uniformity of measurements (in Russian).
[3] Abdullin A I, Idrisov M R, Emelyanycheva E A 2017 Improvement of thermal-oxidative stability of petroleum bitumen using «overoxidation–dilution» technology and introduction of antioxidant additives Petroleum Science and Technology 35(18) 1859-65
[4] Slowik M 2017 Thermorheological Properties Of Styrene-Butadiene-Styrene (SBS) Copolymer Modified Road Bitumen Procedia Engineering 208 145-50
[5] Hao J, Cao P, Liu Z, Wang Z 2017 Developing of a SBS polymer modified bitumen to avoid low temperature cracks in the asphalt facing of a reservoir in a harsh climate region Construction and Building Materials 150 105-13
[6] Zhang D, Chen Z, Zhang H, Wei C 2018 Rheological and anti-aging performance of SBS modified asphalt binders with different multi-dimensional nanomaterials Construction and Building Materials 188 409-16
[7] Galkin A V and Pyrig Y I 2018 Styrene-butadiene-styrene modified low penetration bitumen Bulletin of Kharkov National Automobile and Highway University 83 5-11
[8] Nian T, Li P, Wei X, Wang P, Li H, Guo R 2018 The effect of freeze-thaw cycles on durability properties of SBS-modified bitumen Construction and Building Materials 187 77-88
[9] Schaur A, Unterberger S, Lackner R 2017 Impact of molecular structure of SBS on thermomechanical properties of polymer modified bitumen European Polymer Journal 96 256-65
[10] Bo L, Yujiao C, Xiang L, Hailian L, Xiaomin L 2019 Effect of material composition on nano-adhesive characteristics of styrene-butadiene-styrene copolymer-modified bitumen using atomic force microscope technology International Journal of Adhesion and Adhesives 89 168-73
[11] Xia T, Xu J, Huang T, He J, Zhang Y, Guo J, Li Y 2016 Viscoelastic phase behavior in SBS modified bitumen studied by morphology evolution and viscoelasticity change Construction and Building Materials 105 589-94
[12] Roman C, García-Morales M 2018 Comparative assessment of the effect of micro- and nano-fillers on the microstructure and linear viscoelasticity of polyethylene-bitumen mastics Construction and Building Materials 169 83-92
[13] De Carcer Í A, Masegosa R M, Teresa Viñas M, Sanchez-Cabezudo M, Salom C, Prolongo M G, Contreras V, Barceló F, Páez A 2014 Storage stability of SBS/sulfur modified bitumens at high temperature: Influence of bitumen composition and structure Construction and Building Materials 52 245-52
[14] Laukkonen O-V, Soenen H, Winter H H, Seppälä J 2018 Low-temperature rheological and morphological characterization of SBS modified bitumen Construction and Building Materials 179 348-59
[15] Pat 2618854 Russian Federation, ITUC C08L95/00. Applicant and patent holder Federal State Budgetary Institution of Higher Education "Belgorod State Technological University. Shukhov V G” Publ. 05/11/17 (in Russian)
[16] Das A K and Panda M 2017 Investigation on Rheological Performance of Sulphur Modified Bitumen (SMB) Binders Construction and Building Materials 149 724-32
[17] Ortega F J, Navarro F J, García-Morales M 2017 Dodecylbenzensulfonic Acid as a Bitumen
Modifier: A Novel Approach To Enhance Rheological Properties of Bitumen *Energy & Fuels* **31**(5) 5003-10

[18] Elkholy S A, Abd El-Rahman A M M, El-Shafie M, Abo-Shanab Z L 2018 Physical and rheological properties of modified sulfur asphalt binder *International Journal of Pavement Research and Technology*

[19] Saltan M, Terzi S, Karahancer S 2018 Performance analysis of nano modified bitumen and hot mix asphalt *Construction and Building Materials* **173** 228-37

[20] Loise V, Vuono D, Policicchio A, Teltayev B, Gnisci A, Messina G, Oliviero Rossi C 2019 The effect of multiwalled carbon nanotubes on the rheological behaviour of bitumen *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **566** 113-9

[21] Yang Q, Liu Q, Zhong J, Hong B, Wang D, Oeser M 2019 Rheological and micro-structural characterization of bitumen modified with carbon nanomaterials *Construction and Building Materials* **201** 580-89

[22] Hussein A A, Jaya R P, Abdul Hassan N, Yaacob H, Huseien G F, Ibrahim M H W 2017 Performance of nanoceramic powder on the chemical and physical properties of bitumen *Construction and Building Materials* **156** 496-505

[23] Farias L G A T, Leitinho J L, de C Amoni B, Bastos J B S., Soares J B, de A Soares S, de Sant’Ana H B 2016 Effects of nanoclay and nanocomposites on bitumen rheological properties *Construction and Building Materials* **125** 873-83

[24] Mohammadiroudbari M, Tavakoli A, Aghjeh M K R, Rahi M 2016 Effect of nanoclay on the morphology of polyethylene modified bitumen *Construction and Building Materials* **116** 245-51

[25] Kosma V, Hayrapetyan S, Diamanti E, Dhawale A, Giannelis E P 2018 Bitumen nanocomposites with improved performance *Construction and Building Materials* **160** 30-8

[26] Li L, Wu S, Liu G, Cao T, Amirkhanian S 2017 Effect of organo-montmorillonite nanoclay on VOCs inhibition of bitumen *Construction and Building Materials* **146** 429-35

[27] Ezzat H, El-Badawy S, Gabr A, Zaki E-S I, Breakah T 2016 Evaluation of Asphalt Binders Modified with Nanoclay and Nanosilica *Procedia Engineering* **143** 1260-67

[28] Mansourian A, Goahri A R, Khosrowshahi F K 2019 Performance evaluation of asphalt binder modified with EVA/HDPE/nanoclay based on linear and non-linear viscoelastic behaviors *Construction and Building Materials* **208** 554-63