Preparation of Polymer Bitumen Binder in the Presence of a Stabilizer

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Abstract: The article presents the results of research on the production of polymer-bitumen binder (PBB) based on mixtures of non-oxidized and oxidized petroleum products, namely high-viscosity tar, darkened vacuum distillate, and oxidized petroleum bitumen 70/100, obtained at technological installations of Limited Liability Partnership (LLP) “JV Caspi Bitum” and styrene-butadiene-styrene (SBS) block copolymer brand L 30-01A modifier in the presence of a stabilizer. The results obtained show that the introduction of the SBS modifier in the presence of a sulfur stabilizer improves the performance characteristics of PBB, such as elasticity, ductility, softening temperature, penetration, and brittleness temperature.

Keywords: bitumen; modifier; styrene-butadiene-styrene block copolymer; tar; plasticity; elasticity; penetration; ductility

1. Introduction

With insignificant transport loads, conventional building materials can provide an acceptable quality of work for several decades, but recently this situation has changed dramatically. There are more and more cars, the traffic intensity increases. Accordingly, the load on the road increases significantly. Traditional binder in the form of bitumen can no longer provide the necessary characteristics of the roadway. The specific disadvantages are as follows: high sensitivity to temperature changes; low elasticity; poor mechanical characteristics; ageing property.

Over the past 30 years, research has been continuously conducted to improve the economic efficiency and practicality of using hot bitumen. It was found that, to improve the technological qualities of the traditional binder, it is advisable to use polymeric materials [1]. Modified bitumen obtained by adding a polymer showed a high level of quality indicators: improved performance capability at temperature differences, elastoplastic characteristics, increased fatigue resistance, improved adhesion to fillers, and increased resistance to aging. The specific level of these advantages depends significantly on the type of bitumen and polymer used, as well as on the characteristics of the technological process.

Over the past few years, a variety of polymers have been used as bitumen modifiers, including plastomers such as polyethylene (PE) [1,2], polypropylene (PP) [3,4], polyethylene vinyl acetate (EVA) [5–7], polystyrene-acrylonitrile (SAN) [8], poly ethylene terephthalate (PET) [9], elastomers such as natural rubber (NR) [10], styrene-butadiene rubber (SBR) [11], ethylene-propylene diene rubber [12], etc., thermoplastic elastomers such as polystyrene-butadiene styrene (SBS) [13–15], polystyrene-ethylene/propylene-styrene (SEBS) [16,17], polystyrene-isoprene-styrene (SIS) [18], and nanomaterials [19].

According to the results of studies, these polymers led to some improvements in the properties of bitumen, such as higher stiffness at high temperatures, increased resistance to fracture at low temperatures, improved moisture resistance, and longer service life [2,4,17,20–30].
In the paper [31] the authors showed the possibility of using SBS latex for asphalt modification. At the same time, latex SBS-modified bitumen demonstrated good results in many rheological properties. In addition, the authors [32] revealed a positive effect of trans-polyoctenamer (TOR) on the compatibility and thermal stability of modified CR/SBS asphalt. The current trend in the use of CR and SBS modifiers is their application for processing and modifying aged asphalt into polymer-modified asphalt [33].

The most popular thermoplastic elastomer for bitumen modifiers is styrene-butadiene-styrene block copolymer. Thermoplastic elastomers can withstand permanent deformation under tension and recover elastically after removal of the load [34]. SBS copolymers consist of styrene-butadiene-styrene triple chains with a two-phase morphology of stiffened polystyrene domains (dispersed phase) in a flexible polybutadiene matrix. The chemical bond between the polystyrene (PS) and polybutadiene (PB) blocks can immobilize the domains in the matrix. The $T_g$ of PS blocks is about $+95 \, ^\circ C$ and the $T_g$ of PB blocks is about $-80 \, ^\circ C$ [35].

Polystyrene blocks are responsible for the strength of polymers, while polybutadiene blocks give elasticity. In normal operating temperatures, road bitumen PS blocks are vitreous and contribute to the strengthening of SBS, while PB blocks are elastic [36]. In addition, the incompatibility between polystyrene (PS) and polybutadiene (PB) blocks makes it possible to physically cross-link PS blocks. This aggregation of PS blocks disappears at high temperatures when the kinetic energy of molecular thermodynamic motion is greater than the energy of intermolecular interaction [37]. However, the physical crosslinking among the PS blocks can be reformed and the strength and elasticity of the SBS can be restored after cooling, which is a very important factor for the SBS.

After adding SBS copolymers to the bitumen, some interactions occur between the bitumen and the SBS. In the work [38] it was shown that intermolecular interactions between bitumen and PB are stronger than with PS. The authors believed that PB blocks interact with positively charged bitumen groups through their $\pi$ electrons, while PS blocks interact with electron-rich bitumen groups through their aromatic protons.

PS blocks mixed with bitumen in SBS copolymers absorb part of saturated chains and several rings in light bitumen components, which leads to inturgescence of PS blocks and strengthening of bitumen [39,40]. When the polymer content is low, SBS is dispersed as a discrete phase into bitumen [39]. As the concentration of SBS increases, the inversion phase begins in modified bitumen [41,42].

This ideally represents two blocked external phase: the bituminous-enriched phase and the SBS-enriched phase. In the SBS-enriched phase, there are two subphases: turgent-matrix PB and practically pure PS domains [39]. Once the SBS-enriched phase is formed, an elastic network is formed in the modified bitumen, which leads to an increase in the complex modulus and viscosity, improves elasticity, and increases fracture resistance at low temperatures.

The use of a bitumen base with insufficient brittleness temperature (for example, bitumen obtained only by oxidation) for modification can lead to poor quality of the final product. One of the promising and effective methods of obtaining petroleum bitumen is a technology based on the mixing of deeply oxidized bitumen with heavy oil residues (“oxidation-compounding”). Recently, this technology has been introduced at some bitumen plants in Kazakhstan. It allows to expand the range of products, improve the properties of petroleum bitumen, and reduce environmental pollution.

To select the most preferred method of obtaining petroleum bitumen with improved properties by the technology of “oxidation-compounding,” special research is needed to develop formulations and technologies for their production, taking into account the nature of the processed raw materials and the specific conditions of a particular refinery. Compounded bitumen is obtained by mixing residues from the processing of crude oil. In the technology of compounding bitumen, additives such as oil, tar, light oil fractions are often used, since with their help bitumen with desired properties is obtained, which cannot be done by deep vacuum stripping or oxidation.
Today, at LLP “JV CASPI BITUM”, petroleum road bitumen is obtained using compounding technology, mixing oxidized bitumen with vacuum column tar. This decision was made due to the fact that the shortcomings of the design scheme for the production of road bitumen do not allow working on two columns at the same time. This research can be extended to other common refineries around the world with the correct choice of bitumen tar ratios.

The aim of the research was to study the possibility of obtaining a polymer bitumen binder corresponding to the norms of standards of Kazakhstan STRK 2534-2014 on the basis of mixtures of non-oxidized and oxidized petroleum products, namely high-viscosity tar, darkened vacuum distillate, and oxidized petroleum bitumen PB 70/100, obtained on technological installations LLP “JV Caspi Bitum” from the Karazhanbas oil field and styrene-butadiene-styrene block copolymer (brand SBS L 30-01A) modifier in the presence of a stabilizer.

2. Materials and Methods

Raw materials and reagents were used: tar from the company LLP “JV Caspi Bitum”, darkened vacuum distillate (DVD), and modifier–thermoplastic elastomer brand SBS L 30-01A (powder production of JSC “Voronezhsintezkauchuk”, sulfur (LLP “Atyrau refinery”).

The characteristics of the feedstock for the preparation of modified bitumen samples are given in Table 1.

| Item                                      | Tar #1 | Tar #2 | Test Method             |
|-------------------------------------------|--------|--------|-------------------------|
| Depth of penetration, 0.1 mm, at 25 °C    | 95     | 110    | Standard of RK 1226     |
| Ductility, cm, at 25 °C                  | >150   | >150   | Standard of RK 1374     |
| Ring-and-ball softening point, °C        | 42.7   | 43.1   | Standard of RK 1227     |
| Dynamical viscosity, at 60 °C            | 132.5  | 104.2  | Standard of RK 1211     |
| Kinematic viscosity, at 135 °C           | 314.6  | 341.9  | Standard of RK 1210     |
| Brittleness temperature on Fraass, °C    | −14    | −16    | Standard of RK 1229     |
| Flashpoint, °C                           | 296    | 298    | Standard of RK 1804     |
| Mass variation                           | 0.05   | 0.08   | Standard of RK 1224     |
| Change of softening temperature          | 4.7    | 5.4    | Standard of RK 1227     |

Characteristics of reagents for preparation of modified bitumen samples are given in Table 2.

| Item                                      | Modifier Thermoplastic Elastomer Brand SBS L 30-01A |
|-------------------------------------------|-----------------------------------------------------|
| Structure                                  | linear                                              |
| Content of bound styrene, %               | 30                                                  |
| Hardness on Shor, nominal unit            | 80                                                  |
| Mass fraction of volatile substances, %   | 0.8                                                 |
| Mass fraction of ash, %                   | 0.3                                                 |
| Specific gravity                          | 0.95                                                |
| Nominal strength tensile, MPa             | 21                                                  |
| Melt flow index, 200 S/5 kgs              | 1                                                   |

To modify the bitumen in the laboratory were used mixing equipment consisting of laboratory emulsifier BME 100LT, agitator, thermometer.
According to the method developed by LLP “JV CASPI BITUM”, to the tar heated to 180–185 °C was added ZVF, and this was mixed in a colloid mill. Next, the calculated amount of polymer is added and mixed at a speed of 3200 revolutions per minute for 30 min to disperse the polymer in the tar. Since the dissolution efficiency is greatly influenced by the size of polymer particles, the higher the dispersion (grinding) of polymer particles, the greater the specific contact surface of it with bitumen, the faster the process of swelling and, accordingly, the dissolution of the polymer in bitumen. When preparing PBB, optimal temperature selection is extremely important. Increasing the temperature increases the mobility of the chains of polymer macromolecules and the distance between them. This facilitates the swelling process. The optimal temperature at which the macromolecules of SBS-type polymers are located at the maximum distance from each other corresponds to the temperature of the viscous state and is 180–190 °C. However, an increase in the temperature of PBB preparation above the working technological temperature for road bitumen causes bitumen aging. The mixture is then transferred to a stirrer at a stirring speed of up to 600 rpm and stirred for 1 h to create a homogeneous mixture. Next, sulfur is added to the mixture to stabilize the polymer-bitumen dispersion, and mixing of the mass continues for 1.5 h.

**Determination of Physical and Mechanical Characteristics of Bitumen**

Physical and mechanical characteristics of bitumen, such as elasticity, softening temperatures for the ring and ball, determination of the depth of penetration of the needle, and fragility temperature for Fraass were determined using the methods [43].

### 3. Results and Discussion

To select the optimal concentration of the modifier, were carried out laboratory studies of PBB at different concentrations of the modifier. To obtain a polymer-bitumen binder was used modifier-SBS (styrene-butadiene-styrene block copolymer brand SBS L 30-01A). At the beginning of the study, a residual bitumen base in the form of high-viscosity tar and darkened vacuum distillate (DVD) was used as a raw material. At many modern oil refineries, there is a tendency to increase the depth of selection of distillate fractions from fuel-oil residual during vacuum distillation in order to increase the depth of crude oil refining. This leads to a significant increase in the viscosity of the resulting tar, which according to numerous studies is not the optimal raw material for the production of bitumen by oxidation. Road binders based on such raw materials are often characterized by reduced elongation values at 0 °C and penetration at 0 °C, as well as increased brittleness temperature. As a consequence, in order to optimize the composition of the raw material for the production of oxidized bitumen, it is possible to add to its composition various high-boiling petroleum products, in particular DVD.

After addition to the residual bitumen base SBS (styrene-butadiene-styrene block copolymer brand SBS L 30-01A) were investigated the following operating characteristics of polymer bitumen binder, such as the depth of penetration, the softening point by the ring and the ball, brittleness temperature on Fraass, and elasticity.

The test results of the modified bitumen are shown in Figures 1 and 2 and Table 3.

When SBS is added to bitumen, its physical and mechanical properties change, with increasing concentration the operating temperature interval significantly increases, the binder becomes elastic and plastic at positive and negative temperatures, the adhesion of the mineral material to the binder improves. PBB based on styrene-butadiene-styrene (SBS) type thermoelastoplast, unlike bitumen along with the coagulation frame of asphaltene complexes, contains an additional elastic structural network of macromolecules of SBS type block copolymer which determines the difference between its properties from the properties of bitumen. Increasing the polymer content increases the strength of the structural network, accordingly increases the elasticity and heat resistance of the binder and due to the orientation effect of its flexibility and crack resistance at low temperatures.
Penetration decreases with increasing polymer content (Figure 1). Polymers absorb bitumen oils and form a separate dispersed phase, which leads to a decrease in the oil/asphaltene ratio, resulting in an increase in viscosity and an increase in the indurate of the binder.

A high concentration (more than 5%) of SBS is undesirable for PBB, because the binder becomes excessively viscous, a fairly high temperature is required to soften it, and such PBB is difficult to use for the preparation of asphalt concrete mixture at the plant. As can be seen from the data of Figure 3, the characteristics of the depth of penetration, stability to foliation deteriorate. Thus, the optimal concentration of SBS is 5%.

![Figure 1](image1.png)

Figure 1. Dependence of depth of penetration (1), ring and ball softening point (2), elasticity (3) on SBS concentration.

![Figure 2](image2.png)

Figure 2. Dependence of brittleness temperature on Fraass on SBS concentration.

### Table 3. The test results of the modified bitumen at different concentrations of the modifier.

| No. | Item                              | Tar #1 + DVD (2.5% wt.) | Tar #1 + DVD (2.5% wt.) + SBS (1% wt.) | Tar #1 + DVD (2.5% wt.) + SBS (3% wt.) | Tar #1 + DVD (2.5% wt.) + SBS (5% wt.) | Tar #1 + DVD (2.5% wt.) + SBS (7% wt.) |
|-----|-----------------------------------|-------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| 1   | Ductility, cm, at 25°C            | >150                    | >150                                   | >150                                   | >150                                   | >150                                   |
| 2   | Flashpoint, °C                    | 296                     | 277                                    | 280                                    | 284                                    | 305                                    |
| 3   | Stability to foliation, % no more than | 2                        | 2                                      | 2                                      | 2                                      | 1                                      |
| 4   | Homogeneity                       | -                       | homogenous                             |                                        |                                        |                                        |

![Table 3](image3.png)
Laboratory studies of PBB were carried out to optimize the formulation for the purpose of preparation different grades of PBB with improved characteristics corresponding to the norms of ST RK 2534-2014 (standard of Republic of Kazakhstan). To obtain PBB, two samples of raw materials were taken: tar #1 and tar #2. The polymer was taken at an optimal concentration of 5%. The test results are shown in Table 4.

### Table 4. The results of the test of modified bitumen.

| No. | Items                                      | ST RK 2534-2014 | PBB 70–100 | Tar #2 + DVD (2.5% wt.) | Tar #2 + DVD (2.5% wt.) + SBS (5% wt.) |
|-----|--------------------------------------------|-----------------|------------|-------------------------|----------------------------------------|
| 1   | Depth of penetration, 0.1 mm, at 25 °C      | 71–100          | 110        | 92                      |                                        |
| 2   | Ductility, cm, at 25 °C                    | 25–30           | >150       | >150                    |                                        |
| 3   | Ring-and-ball softening point, °C          | 58–60           | 41.9       | 70.8                    |                                        |
| 4   | Brittleness temperature on Fraass, °C      | From −20 to −18 | −16        | −20                     |                                        |
| 5   | Elasticity, %, at 25 °C                    | >60             | -          | 96.9                    |                                        |
| 6   | Flashpoint, °C                             | 230–235         | 298        | 306                     |                                        |
| 7   | Stability to foliation, % no more than     | 2               | 2          | 2                       |                                        |
| 8   | Homogeneity                                | homogenous      | -          | homogenous              |                                        |

As can be seen from Table 4, the actual PBB values for sample 1, such as softening point, is 61.5 °C, brittleness temperature on Fraass is −20 °C, penetration at 25 °C is 92 mm, ductility at 25 °C is ≥ 150 cm, elasticity at 25 °C is 94.1%; for sample 2, softening point is 70.8 °C, brittleness temperature on Fraass is the same as in sample 1, penetration at 25 °C is 110 mm, ductility at 25 °C is ≥ 150 cm, and elasticity at 25 °C is 96.9%. Both samples are homogenous and meet the requirements of ST RK 2534-2014.

It has been stated above that the operating characteristics of bitumen can be improved if an oxidized residual bitumen base is used to prepare a polymer bitumen binder. Therefore, the influence of changes in the parameters of modified bitumen from the mass content of petroleum road bitumen (PRB 70/100) was studied. Test conditions: PRB 70/100, 4 h, 5% SBS-modifier, T = 180–185 °C (Figures 3 and 4 and Table 5).

Comparative analysis showed that, when PRB 70/100 bitumen is added to the raw material up to 30%, there is a slight improvement in the quality of PBB in all indicators except for the index of brittleness temperature and penetration. As seen from the figure, the addition of more than 20% of petroleum road bitumen PRB 70/100 will lead to a decrease
in penetration and an increase in ring and ball softening point and elasticity. Therefore, we consider the optimal concentration of petroleum road bitumen to be 20%.

![Figure 4. Dependence of brittleness temperature on Fraass on petroleum road bitumen concentration.](image)

**Table 5.** The test results of the modified bitumen at different concentrations of the petroleum road bitumen.

| № | Item                      | Raw Material | ST RK 2534-2014 PBB 70-100 |
|---|---------------------------|--------------|----------------------------|
| 1 | Ductility, cm, at 25 °C   | 25–30        | >150 (>150)                 |
| 2 | Flash point, °C           | 230–235      | 296 (284)                  |
| 3 | Homogeneity               | homogenous   | -                          |

Sulfur and its compounds are used to stabilize the polymer-bitumen dispersion. Between the polymer and sulfur reactions occur, resulting in new chemical compounds, they remain evenly distributed in the bitumen due to its lattice structure. Sulfur vulcanization is a chemical process widely used in the production of technical rubbers, it makes it possible to improve the storage stability of some PBBs (for example, SBS modified bitumen) [44–49]. It is believed that sulfur works in two directions: chemically crosslinking polymer molecules and chemically binding polymer and bitumen through sulfide and or polysulfide bonds [45]. These chemical interactions are much stronger than physical ones (e.g., aggregation of PS blocks into copolymers), and they do not disappear even at fairly high temperatures, which is thought to be very useful for improving stability during PBB storage. The crosslinking of polymer molecules results in the formation of a stable interpenetrating polymer networks in bitumen; while the connection between polymer and bitumen directly reduces the possibility of separation. In addition to increased storage stability, some researchers [50–53] have argued that sulfur vulcanization can also improve the elasticity, deformation resistance, and some rheological properties of PBB.

In connection with the above, the influence of changes in the parameters of modified bitumen from the mass content of the stabilizer in the initial mixture (80% tar + 20% bitumen) was studied. Test conditions: petroleum road bitumen PRB 70/100, 4 h, 5% SBS-modifier, T = 175 °C (Figures 5 and 6 and Table 6).
Figure 5. Dependence of depth of penetration (1), ring and ball softening point (2), elasticity (3) on stabilizer concentration.

Figure 6. Dependence of brittleness temperature on Fraass on petroleum road stabilizer concentration.

Table 6. The test results of the modified bitumen at different concentrations of the stabilizer.

| №№ | Item | Raw Material | The Composition of the Samples, % |
|-----|------|--------------|----------------------------------|
|     |      | ST RK 2534-2014 PBB 70–100 | Petroleum Road Bitumen PRB 70/100 |
| 1   | Ductility, cm, at 25°C | 25–30 | >150 | >150 | 149.0 | 133.5 | 92.9 | 73.7 |
| 2   | Flash point, °C | 230–235 | 296 | - | 258 | 248 | 246 | 238 |
| 3   | Homogeneity | - | - | - | homogeneous |
Comparative analysis showed that, when the stabilizer is involved in the raw material up to 0.25%, there is an improvement in the quality of PBB in all indicators. With an increase in the fraction of the stabilizer in the PBB to 0.5%, some operating characteristics deteriorate.

4. Conclusions

Herein, we have shown the possibility of obtaining bitumen corresponding to the norms of ST RK 2534-2014 (standard of Kazakhstan) on the basis of mixtures of non-oxidized and oxidized petroleum products, namely high-viscosity tar, darkened vacuum distillate, and oxidized petroleum road bitumen PRB 70/100 obtained on technological installations of LLP “JV Caspi Bitum” from the oil field Karazhanbas.

The obtained PBB were analyzed by physical and mechanical parameters for compliance with ST RK 2534-2014 “Polymer-bitumen binders for roads on the basis of block copolymers of styrene-butadiene-styrene type”.

Studies have shown that, when using a polymer modifier SBS at a concentration of 5%, the addition of PRB to 20%, stabilizer to 0.25%, there is an improvement in the quality of PBB on all indicators.

The results of the tests on the selection of the polymer-bitumen binder formulation will be used at the modified bitumen plant intended for the production of polymer-modified road bitumen from the vacuum residue of Karazhanbass oil (tar) from the electrical desalting plant, atmospheric-vacuum pipe still (EDP AVPT), and SBS thermoelastoplast (styrene-butadiene-styrene block copolymer). The design capacity of the plant is approximately 120,000 tons per year of modified bitumen.

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