Original Article

Studying of Properties of Bitumen Modified based on Secondary Polymer Wastes Containing Zinc


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Abstract - This paper uses laboratory experiments to present the properties of zinc-containing secondary polymer (ZnIP) and sulfur-containing modified bitumen. Zinc chloride is used as the main raw material, acrylonitrile as secondary polymer monomers, tri polymers based on isoprene, natural rubber, and styrene. BND 60/90 potential base bitumen is mixed with zinc-preserved secondary polymer (ZnIP) and sulfur in various proportions using a high-shear laboratory-type mixer. The properties and microstructure of the samples determined by conventional and empirical testing methods, IR-spectrum, SEM analysis (Scanning Electron Microscope), elemental analysis, thermal gravimetric (TGA and DTA) analysis, and X-ray phase analysis are studied. The results showed that zinc-containing secondary polymer (ZnIP) and sulfur modification improved the traditional properties of base bitumen, such as a positive change in softening point, temperature sensitivity, etc. The microstructure and properties of zinc-containing secondary polymer (ZnIP) and sulfur-modified bitumen depend on the type of secondary polymer, the solubility of the second polymer in the bitumen, and the composition of the second polymer. The results of the above analysis showed that the physicochemical, viscosity, elasticity, and rheological properties of bitumen modified based on ZnP-S gave very good results compared to unmodified bitumen. Experiments were conducted proving that bitumen modified based on ZnP-S increases the elasticity, heat, cracking, and long-term resistance of asphalt.

Keywords - Bitumen, Sulfur-modified bitumen, Acrylonitrile, Isoprene rubber, Styrene, IR-spectrum, Scanning Electron Microscope.

1. Introduction

At the current time, in many developed and developing countries, the road system is of great importance, mainly due to the increase in the volume of heavy vehicles and the significant increase in the permissible weight of these vehicles. The impact on vehicles led to a sharp increase in the carrying capacity. As a result of this, due to a sharp increase in the stress acting on the bitumen surface, most of the road system is damaged and deteriorated as a result of the short service life. Certain conditions, such as different environments, climates, heavy traffic, and tire pressures, cause various surface defects in asphalt pavements. Examples of common causes of damage to road surfaces are permanent deformation at high temperatures, fatigue cracks at intermediate temperatures, and thermal cracks at low temperatures.

Currently, the quality of bitumen is improved by adding various additives to prevent or reduce the deterioration of asphalt pavements. Asphalt pavements' densification is significantly influenced by the low and high-temperature indicators of binders. Therefore, in recent years, many natural and chemical additives have improved some properties of traditional bitumens, such as aging stability, heat sensitivity, elastic behavior, and crack resistance. The use of polymer-based additives in bitumen modification has increased significantly. Also, two main types of polymers, elastomer and elastomer, are widely used. Plastomers are commonly used to improve the elastic properties of binders and increase the resistance to permanent deformation of coatings. However, elastomers have been used to improve the fatigue and low-temperature cracking resistance of binders. In order to study the effect on the physical and chemical properties of soft consistency bitumen, studies are being conducted on the use of secondary products, which are elastomeric polymers and sulfur as a bitumen additive.

Tripolymers are used as secondary polymers, which are polymers containing functional groups that can form chemical bonds with some bitumen components. These polymers form a network around asphaltene contained in bitumen, forming an integral compound and exhibiting the ability to chemically react with bitumen. However, when these chemical bonds occur, in this case, a polymer bitumen mixture that does not have melting and solvent properties and is generally useless can be formed. Therefore, terpolymers and sulfur content used in bitumen modification should have a high limit for their properties to lower the gel point in terms of the chemical composition of the main network.
In some studies, this limit is estimated to be 5-5.5% by weight, although it is noted that this figure could be less than 1% [13, 14]. Some literature suggests that bitumen containing less tri polymer group and sulfur can achieve much better results. In addition, using a larger amount of tri-polymer leads to economic disadvantages [15].

When ZnIP and sulfur are used in bitumen modification, potassium persulfate or Polyphosphoric Acid (PPA) is usually used as a catalyst to accelerate the chemical reaction between bitumen and polymer in the mixture [16], the amount of ZnIP-S required in bitumen-ZnIP-S mixture modification as a result of a certain amount of reduction. It was observed that the resistance properties of modified bitumen to permanent deformation, wear, compression, and cracking increased to a certain extent [17-18].

At present, in addition to ZnIP-S elastomeric polymers, Styrene-Butadiene-Styrene (SBS) is followed by styrene-butadiene rubber, ethylene vinyl acetate, and polyethylene are used in bitumen modification. The use of synthetic polymers to extend the service life and change the composition of traditionally used bituminous binders dates back to the early 1970s [19]. When using synthetic polymers, bituminous binders have reduced temperature resistance, increased degradation, and rheological properties [20, 21]. The global distribution of different types of modified bituminous binders is 75% elastomer, 15% elastomer, and 10% recycled crumb rubber and other modifiers (e.g., sulfur) [22].

Within the elastomeric group, styrene tri-polymer show the greatest potential when mixed with bitumen [23]. Other types of elastomers used in bitumen modification include natural rubber, polybutadiene, polysoprene, isobutene isoprene copolymer, polychloroprene, and styrene butadiene rubber. Styrene tri polymers, which can combine elastic and thermoplastic properties, called thermoplastic rubbers, can be produced by sequential polymerization of styrene acrylonitrile isoprene (SAI) [24].

Alternatively, diblock precursor styrene and midblock monomers may be produced by sequential polymerization of acrylonitrile and polysoprene followed by a reaction with a coupling agent [25]. Therefore, not only linear copolymers but also 4 polyhedral copolymers (star, radial, or network copolymers) can be produced. Therefore, the structure of SAI tri polymer consists of styrene polyacrylonitrile polysoprene tri-block chains with a two-phase morphology of spherical polystyrene block domains within a polysoprene matrix [26].

In many experiments conducted to determine the elasticity, mass loss, or wear resistance of bitumens modified with tri-polymer, it is found that bitumen modified with Zn-SAI-S has a very positive effect on elasticity and wear resistance [27]. Studies have shown that the modified bitumen's internal structure is homogeneously distributed due to the reaction between the metal and the binder, and the cracking problems may occur between them have disappeared [28].

In addition, many studies have shown that the addition of tri polymer to bitumen leads to an increase in the complex modulus of modified bitumen but a decrease in its phase angle; that is, bitumen modified with Zn-SAI-S improves the cracking resistance of pavements provides [29]. When the rheological properties of bitumen modified with different polymers were studied at low temperatures, it was found that the cracking resistance of bitumen modified with Zn-SAI-S is lower than that of other bitumens [30]. However, some studies have found that using tri-polymer in bitumen modification increases the high-temperature performance of the modified bitumen without significantly affecting the low-temperature performance [31, 32]. The study results showed that the hardness of modified bitumen increased, and the temperature sensitivity decreased due to the increase in the amount of additives. In addition, although the low-temperature performance of modified bitumens is relatively low, their high-temperature performance is significantly increased.

2. Experimental Part

BND 60/90 brand GOST 22245-90 bitumen (GOST 127-93) tri-polymer containing sulfur and zinc were used for bitumen modification. We can prepare a tri-polymer containing zinc to modify the bitumen previously obtained as modifiers. 100 ml of distilled water, 20 g of zinc chloride salt, 110 ml of styrene, and 50 ml of acrylonitrile were poured into a round-bottomed flask; while gently stirring, 20 g of sodium alkali was added to remove chlorine from the mixture. The flask is placed on a magnetic stirrer and heated. The temperature increased from 70 °C to 110 °C. In order to activate the polymerization process, an initiator, 0.05 g of potassium persulfate, was added. As a result of the reaction, a whitish-yellow, sticky, high-viscosity substance was obtained. Isoprene, natural rubber, was added to this substance and heated at 120 °C with stirring. 350 grams of bitumen placed in a 1000 ml container with a high thermal temperature resistance and heated at 135-180°C temperature until it liquefies by gradually increasing the heat. After liquefaction, 97.5 g of sulfur and 52.5 g of yellow elastic substance were added. Reaction mixed and cooled at a temperature of 120-135°C for 1-2 hours. The properties of the modified bitumen were obtained.

3. Results and Discussion

3.1. IR-Spectrum of Modified Bitumen based on ZnIP-S

IR-spectra analyzes of modified bitumen based on ZnIP-S and unmodified bitumen were obtained on Specord-75 IR spectrograph device. Spectra were performed from 500 to 4000 cm⁻¹ at the same intensity and the same scanning speed (Fig. 1). IR-spectra of unmodified bitumen (in red) and IR-spectra of modified bitumen based on ZnIP-S (in black) are shown.

The IR-spectrum of bitumen modified based on ZnIP-S and unmodified bitumen was compared. The region of 2920.23 cm⁻¹ obtained at high intensity, the vibration of -CH₃ and –CH₂ chains connected in a straight chain was observed. 2850.79-2852.72 cm⁻¹ indicates a C-H alkane chain. In the 1620.21 cm⁻¹ region, a C=O chain connected in
a straight chain and an aromatic ring was observed. Branched S-S valence vibrations were observed in the region of 1375.25 cm\(^{-1}\). The -S=N chain in acrylonitrile was observed in the region of 1120.64 cm\(^{-1}\). We can see that the C=O carboxylic functional group appeared in the 1035.75 cm\(^{-1}\) area. The compositionally bound zinc chloride salt is bound to nitrogen in the area of 736.81 cm\(^{-1}\). It can be seen from the results of the IR-spectrum analysis that ZnIP-S-based modified bitumen was formed as a result of the complete reaction of the initial substances. The general structure of modified bitumen based on ZnIP-S is presented in (Fig. 2).

![Fig. 1 IR spectrum of unmodified and ZnIP-S modified bitumens](image1)

![Fig. 2 Modified bitumen based on ZnIP-S (a) Chemical structure and (b) 3D view model](image2)
Fig. 3 SEM analysis of unmodified bitumen (a) 10 (b) 100 and energy dispersive spectroscopy (c) 15 keV analysis results.

Fig. 4 SEM analysis of modified bitumen based on ZnIP-S (a) 10 (b) 100 and (c) energy dispersive spectroscopy analysis results at 15 keV.
3.2. Scanning Electron Microscope (SEM) and Elemental Analysis

With the help of Scanning Electron Microscope (SEM) and elemental analysis, 10µm and 100µm surface parts of unmodified bitumen and bitumen modified based on ZnIP-S were compared and analyzed. (in pictures 2, 3, 4, 5) and percentages of elements are shown in Table 1. General and separate results of SEM analysis of the elements in unmodified and modified bitumen based on ZnIP-S with dimensions of 50 µm (Figures 5,6) are presented.

![IMG1](image1)

(a) C-K O-K Al-K S-K

![IMG1](image2)

(b) C-K N-K O-K Al-K S-K D-K Zn-K

Fig. 5 The results of the general (a) and separate SEM (b) analysis of the elements of the composition of unmodified bitumen with a size of 50 µm are presented

Fig. 6 Results of general (a) and individual SEM (b) analysis of the 50 µm size of the elements contained in bitumen modified based on ZnIP-S are presented
Table 1. Mass amounts and atomic mass amounts of elements in unmodified and ZnIP-S modified bitumens (in percent).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mass%</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>92.80</td>
<td>95.69</td>
</tr>
<tr>
<td>O</td>
<td>3.84</td>
<td>2.97</td>
</tr>
<tr>
<td>Al</td>
<td>0.48</td>
<td>0.22</td>
</tr>
<tr>
<td>S</td>
<td>2.88</td>
<td>1.11</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
<td><strong>100</strong></td>
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<table>
<thead>
<tr>
<th>Elements</th>
<th>Mass%</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>73.83</td>
<td>87.62</td>
</tr>
<tr>
<td>N</td>
<td>0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>O</td>
<td>1.38</td>
<td>1.23</td>
</tr>
<tr>
<td>Al</td>
<td>0.41</td>
<td>0.22</td>
</tr>
<tr>
<td>S</td>
<td>23.29</td>
<td>10.35</td>
</tr>
<tr>
<td>Cl</td>
<td>0.40</td>
<td>0.16</td>
</tr>
<tr>
<td>Zn</td>
<td>0.36</td>
<td>0.08</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
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</table>

It can be seen from the analysis of the results that the results of SEM and elemental analysis of the surface parts show that the porosity level of bitumen modified based on ZnIP-S is higher than that of unmodified bitumen, that is, the starting materials are completely connected to each other, the materials it can be seen that there are no additives and that the elements are interconnected.

3.3. Thermogrammetric Analysis (TGA) and Differential Thermal Analysis (DTA) of Modified Bitumen based on ZnIP-S

The thermal stability of bitumen modified based on ZnIP-S is one of the important properties that should be obtained to extend their service life.

This study investigated the thermal stability of ZnIP-S modified bitumen based on TGA and the main characteristics of the curves, including the onset temperatures of the mass loss effect. Peak temperatures were calculated from TGA and DTA curves.

The results of the thermogravimetric experiment for modified bitumen based on ZnIP-S were studied on a 6 mg sample in the temperature range of 20-900 °C in an air atmosphere (Fig. 7).

In the DTA analysis of bitumen modified based on ZnIP-S, the mass loss occurred in three areas, and one exothermic and one endothermic process occurred. At the first stage of decomposition of substances, a weight loss of 0.011mg or 0.099 was observed at a temperature of 77.08°C. At this stage, the release of water vapor bound in the form of crystalline hydrate was observed.

In the second stage, 3.286 mg, 30.726% mass loss was observed at 260.81°C. Carbon (II) oxide was released as a result of the decomposition of carboxyl groups in this range of temperatures.

The third stage is the main decomposition stage, starting at 440.31 °C and ending at 877.7 °C, 4.648 mg, and 43.458% mass loss was observed. It was observed that oxides of amino groups of nitrogen and metal oxides were released from the decomposition of metal carbonates from the decomposition of organic compounds.

In the DTA analysis of the synthesized product, it can be seen that 2.751 mg or 25.725% of residual substances remained at 802.34 °C during the absorption of heat, i.e. endothermic process. At this stage, it can be observed that the remains of metal salts remain.

Fig. 7 Thermogravimetric (TGA) and differential thermal analysis (DTA) of modified bitumen based on ZnIP-S
It can be seen that significant consistency of the graph pattern with large peaks was observed for the bitumen sample modified based on ZnIP-S. The bitumen sample modified based on ZnIP-S has two large peaks: the first one appears with $d = 3.68$ at $20^\circ$ 2 th and the second one with $d = 5.74$ at $27^\circ$ 2 th. Generally, the value of "d" represents the width of the peak, which indicates the size of the crystal. The presence of a high peak indicated that the atom is located in a periodic mass and thus recognized as a crystal structure. From the results of the X-ray phase graph, it can be seen that there were complete bonding reactions between the initial substances in the bitumen modified based on ZnIP-S.

4. Conclusion

Today, we can observe small cracks on the roads due to the movement of heavy goods vehicles and the falling rains standing on the asphalt surface. Environmental problems may be the reason why asphalt layers lose their quality so quickly. It can be assumed that the falling rain dissolves the acidic oxides in the air and turns into acid rain. These rains create an aggressive environment in the broad areas where they remain for a long time and increase the reaction ability.

For this purpose, the resistance of our composite bitumen to such inconveniences caused by natural phenomena was studied. The resistance of our compound to acids and alkalis was studied. It was found that it has stable properties. In order to improve the properties of bitumen used in road construction and to extend its service life, when zinc-containing secondary polymer (ZnIP) and sulfur were used, the physicochemical, viscosity, elasticity, and rheological properties of modified bitumen based on ZnIP-S showed very good results compared to unmodified bitumen. ZnIP-S-based modified bitumen road has increased elasticity, heat, cracking, and long-term resistance of asphalt.

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