Preparation of effective nanomodified polymer-bitumen adhesives for asphalt concrete

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Abstract. The possibilities of modification of BNB 50/70 oil road bitumen, which belongs to the category of viscous bitumen and is used in road works in the hot season, at an average temperature not lower than +5°C have been studied. Copolymers of butadiene and styrene and vinyl acetate and ethylene were used as polymer materials for polymer-bitumen adhesives (PBA). A copolymer of butadiene and styrene (SBS) is a synthetic rubber in which solid styrene blocks are linked by butadiene "springs". When mixed with bitumen, they create a highly elastic structure. The inclusion of 2.5 - 6.0% SBS in bitumen as a polymer additive increases the softening point and frost resistance of bitumen, gives high flexibility to the organic adhesive, which increases the heat resistance and shear resistance of asphalt concrete. Ethylene vinyl acetate (EVA) copolymer forms a rigid network in modified bitumen and resists deformation. It dissolves very quickly in thermoplastic bitumen at a temperature of 155-180°C, which facilitates the process of preparing PBY for asphalt-concrete. The optimal concentration of polymers for obtaining high heat-resistant and flexible PBY has been determined. Carbon nanotubes act as a functional additive for bitumen. Modified bitumen adhesives and physical-mechanical indicators of asphalt-concrete mixtures made on their basis were studied. It was found that by introducing a small amount of nanocarbon tubes into asphalt-concrete, its shear resistance and strength are significantly increased at different temperatures (from 0 to 50°C).

1 Introduction

Depending on the regions in the republic, the state of road wear is greatly affected by the significant temperature change of the external environment, which manifests itself as a source of permanent structural changes, in addition to the mechanical effect of traffic flow. It is possible to improve the transport and operational condition of the existing road network by solving the problem of the durability of the asphalt-concrete surface in the current conditions where the wear of road surfaces is increasing. For the top layer of the road surface, materials with high strength, shear, crack and water resistance and at the same time more flexibility are required [1, 2].

The problems of road construction are the issues of providing asphalt concrete production with high-quality materials and, above all, with the main component of the asphalt-concrete

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coating - stable bitumen adhesive. Without applying a quality bitumen adhesive, it is difficult to hope for a significant improvement of the physical and mechanical properties of the road, i.e. reaching the European level.

These studies are devoted to solving the pressing problem of increasing the durability of asphalt concrete pavements by developing compositions of high-quality polymer-bitumen binders (PBB) and functionally modified bitumens for asphalt concrete mixtures. The purpose of these studies is to obtain asphalt concrete mixtures with improved structural and mechanical properties and temperature stability. The structure of asphalt concrete must provide high shear and crack resistance during the required service life of the pavement. Therefore, in this work, the set goal is achieved by preparing asphalt concrete mixtures using modified binding materials that determine the material's resistance to the accumulation of various types of defects and deformations.

Currently, polymer-bitumen binders using thermoplastics such as polyethylene, polypropylene, polystyrene, ethylene-vinyl acetate (EVA), polyethylene terephthalate, as well as rubbers based on polybutadiene, chloroprene, ethylene-propylene, styrene-butadiene are widely used styrene (SBS), divinyl styrene and polyurethane [3-8].

The presented experimental work examines the influence of modifiers on the physical and mechanical properties of the binder, as well as the properties of asphalt concrete based on PBB with optimal concentrations. Copolymers of butadiene with styrene and ethylene with vinyl acetate were used as polymer modifiers.

2 Materials and research methods

In the research work, BNB 50/70 brand oil bitumen TS AZ 3536601.242-2015 (production of Baku oil refinery named after H. Aliyev); Europrene SOL T 6302 brand styrene-butadiene block copolymer - from SBS (produced by the Ravenna plant in Italy); from MasterLife PVA-100 (manufactured by BASF); thermoelastoplastic polymer -EVA, which is a copolymer of ethylene and vinyl acetate, was used.

The use of SBS polymer powder allows you to quickly prepare a homogeneous adhesive when mixing components even in laboratory conditions. Large polymer granules are crushed to the molecular level to form a polymer structured network in special equipment equipped with colloid mills.

Ethylene vinyl acetate is a thermoplastic substance obtained as a result of copolymerization of ethylene and vinyl acetate monomer, its composition determines the mechanical properties of the copolymer.

As a functional modifier, multi-walled carbon nanotubes (MWCNT) synthesized in the 28th laboratory of the Institute of Catalysis and Inorganic Chemistry of the Azerbaijan National Academy of Sciences (ANAS) were used. For the first time in Azerbaijan, an expanded laboratory facility for the synthesis of multi-walled carbon nanotubes (MWCNT) from hydrocarbon gas raw materials was installed and put into operation.

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Fig. 1. Unit for the synthesis of multi-walled carbon nanotubes (MWCNT). 1- gas raw material production unit: gas raw material (propane, butane, their mixture) is diluted with argon to the required thickness and fed to the reactor zone at a certain speed. 2- the reactor unit consists of 2 sections of a tube furnace with a quartz reactor inside, each with independent heating. The furnace heats the reactor up to a temperature of 1000^0C. 3- the temperature regulation section of the furnace consists of a temperature regulator that automatically controls and maintains the set temperature in the reactor and two regulators for supplying current to the coil of the furnace. 4- air conditioning unit. 5- vacuum block: the block for creating a vacuum in the reactor is designed for the synthesis of MWCNT at reduced pressures (80-20 kPa). The unit consists of a vacuum pump, a valve and a manometer.

Electron microscopic analysis of multi-walled carbon nanotubes (MWCNT) is shown in figure 2.

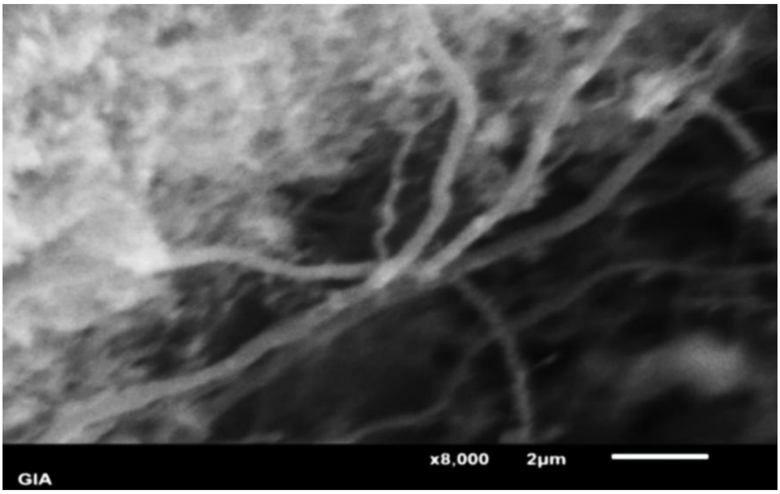


Fig. 2. SEM image of the synthesized MWCNT.

As can be seen from Figure 2, the synthesized MWCNT have a smooth surface, a shape without obvious defects, a straight line, without sharp bends and breaks. This indicator shows both the low defects and high quality of the synthesized MWCNT.

A medium of MasterLife PVA-100 was used to disperse Pomegranate by ultrasonication. MasterLife PVA-100 acted as a carrier of nanodispersed carone nanotubes. Since it is in liquid form, this mixture is incorporated into the bitumen without any further processing.

The preparation of bituminous binder was carried out according to the following technology: in pre-dehydrated and heated bitumen to 160-180°C, the modifier is dosed portionwise in accordance with the given concentration while mixing with a laboratory stirrer at a speed of 100-150 rpm. Then, after 1-2 minutes, mixing begins at a speed of 500-800 rpm until a homogeneous mixture is obtained and the modifier is completely dissolved. The mixing time is 40-60 min, the temperature of the mixture is 165-185°C.

The following research methods were used to study the effect of prepared modifiers on the properties of bitumen and asphalt concrete:

- PBA softening temperature is determined according to the KveSH (GOST 11506-73) method.
- Brittleness temperature is measured according to Fraas (GOST 11507-78).
- The depth of penetration of the needle at 25°C is determined according to GOST 11501-78.
- Adhesion with mineral fillers is determined according to GOST 11508-74.
- The stability of bitumen, which is evaluated according to the change of quality indicators during long-term storage at high temperature (163^{0}C, 5 hours), is carried out according to GOST 18180-72.

3 Research results

The results of studies of the main physical and mechanical properties of binders based on BNB 50/70 bitumen are shown in Table 1.

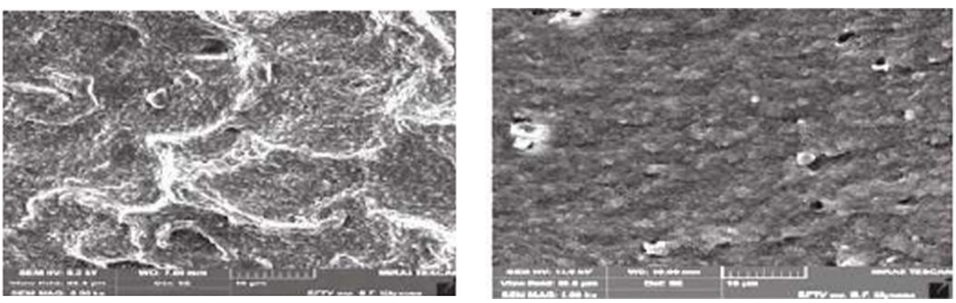
Table 1. Physical and mechanical indicators of original and modified bitumen

Amount of additive, % by weight of bitumen	Softening temperature along the ring and ball, °C	Brittleness temperature according to Fraas, °C	Penetration, 0.1 mm		Extensibility, sm		Adhesion to marble or sand
			at 25 °C	at 0 °C	at 25 °C	at 0 °C	
0	48	-18	84	23	94.1	4.0	satisfactory
1- SBS	53	-20	72	24	95.8	5.7	satisfactory
2- SBS	59	-20	73	26	84.6	6.9	fine
3 - SBS	68	-23	64	27	76.0	13.8	fine
4 - SBS	76	-26	53	25	69.9	22.6	fine
3- EVA	52	-17	66	20	60.5	0.5	satisfactory
4- EVA	58	-17	54	23	97.6	0.6	satisfactory
0.003-MWCNT	55	-19	57	27	32	3	fine
0.005-MWCNT	56	-19	59	28	21	1.6	fine
0.01-MWCNT	60	-18	46	17	15	0.8	fine

When SBS is added to bitumen, its physical and mechanical properties change; with increasing concentration, the operating temperature range significantly increases, the binder becomes elastic and plastic at positive and negative temperatures, and the adhesion of the mineral material to the binder improves. However, a high concentration (more than 4%) of SBS is undesirable for PBA because the binder becomes excessively viscous, requires a fairly high temperature to soften it, and such PBA is difficult to use for preparing asphalt concrete mixtures in a plant. The optimal concentration of SBS is 3%.

EVA copolymer at a concentration of 3-4% expands the temperature range of the bitumen binder. The plasticity of modified bitumen at positive temperatures becomes better than that of pure bitumen, but at 0 ° C the penetration and elongation indicators deteriorate greatly. The EVA modifier in a concentration of more than 4% does not have the best effect on the plasticity of PMB; the brittle temperature indicator worsens, but the resistance to high temperatures improves. Modified MWCNT bitumen has good adhesion and an increased softening point; the binder is plastic at positive temperatures. The MWCNT concentration of 0.003 - 0.005% in bitumen increases the temperature resistance by 1.17 times.

In Fig. Figure 3 shows the microstructure of the asphaltene-resinous complex (ARC) binder without a nanomodifier (it can be seen that the structure is homogeneous and smoothed). But when MWCNTs are introduced into bitumen, the microstructure of the ARC changes noticeably, a peculiar structuring of the ARC occurs around nanoobjects and the structure of the binder becomes more prominent [9].



a b

Fig. 3. Microphotographe's of structure of asphalt resinous bitumen complex, adhesive: a - in presence of MWCNT 0.0005 %; b - without MWCNT

Today, the use of nanocomposites to improve the functional properties of building materials and products is a new promising direction in science and high-tech production. Additions of carbon nanotubes make it possible to obtain composites with improved mechanical properties, including increased strength [9]. Carbon nanotubes are a very light material, but, on the other hand, they have record high specific strength and flexibility. Therefore, MWCNT significantly improve the properties of materials when added in ultra-low concentrations, starting from 0.01% [10]. Carbon nanotubes have high surface energy and therefore tend to form agglomerates, which makes their introduction into various media difficult. In this study, to improve the uniform introduction of MWCNT into the road bitumen matrix, not independent particles, but specially developed MWCNT were used [10].

To monitor the influence of the resulting polymer-bitumen binders and MWCNT-modified bitumens on the properties of road surfaces, which must have strength, wear resistance and water resistance, test batches of asphalt concrete mixtures (ACM) containing mineral components were carried out. For the study, modified bitumens with a minimum sufficient concentration of modifiers were taken: SBS - 3%, EVA - 3%, and MWCNT - 0.005%. ACM was prepared by mixing in a heated state crushed stone, natural crushed sand, mineral powder and binder, taken in ratios determined by the requirements of GOST 9128-2013. The qualitative indicators of ACM are summarized in table 2.

Table 2. Physical and mechanical indicators of hot, close-grained, dense asphalt mixture

Controlled indicators according to GOST 12801-98	4,5% BNB 50/70	4,5% PBA (0,005% MWCNT)	4,5% PBA (3% SBS)	4,5% PBA (3% EVA)
Average density, g/cm^3	2.38	2.38	2.41	2.39
Water saturation, % by volume	3.0	2.7	2.4	2.8
Water resistance	0.91	0.95	0.97	0.94
Crack resistance based on tensile strength during splitting at 0°C, MPa	4.8	4.5	5.3	5.0
Shear stability according to the coefficient of internal friction	0.35	0.91	0.93	0.9
Compressive strength, MPa: - at 50 °C - at 20 °C - at 0° C	 1.2 3.2 6.5	 2.8 4.9 8.4	 2.6 5.7 12.2	 2.7 5.8 12.4

PBA based on a thermoplastic elastomer of the styrene-butadiene-styrene (SBS) type, unlike bitumen, along with a coagulation framework of asphaltene complexes, contains an additional elastic structural network of block copolymer macromolecules of the SBS type, which determines the difference between its properties and the properties of bitumen. In this case, the minimum polymer content at which this network is formed is 2.0-2.5% polymer. Increasing the polymer content increases the strength of the mesh, and therefore the elasticity and heat resistance of the binder and, due to the orientation effect, its flexibility and crack resistance at low temperatures. SBS is the most popular bitumen modifier for various applications.

Thermoplastic based on EVA changes the rheological properties of road bitumen, which in the composition of ACM have a positive effect on indicators such as water, crack and shear resistance (Table 2). When producing asphalt concrete mixtures, without preliminary preparation of modified bitumen, this modifier can be applied directly to the hot stone material in the asphalt concrete mixer at any type of asphalt concrete plant (ACP).

A study of the influence of nanomodified bitumen binders on the strength and deformation properties of asphalt concrete (Table 2) showed that nanotubes act as a cross-linking agent and the use of such modified binders in asphalt concrete mixtures helps to increase the water resistance of asphalt concrete by 1.04 times, shear resistance by 2.86 times, as well as tensile strength at temperatures from 0 to 50°C. The use of MWCNT is possible by directly mixing them with bitumen binder in a tank at an asphalt concrete plant before preparing ABC.

4 Conclusions

Based on SBS, it is possible to prepare high-quality polymer-modified bitumen (PMB) that meets the requirements of the standard. Asphalt prepared using such PMB has fairly high water and crack resistance compared to pure BNB and the PBA discussed above. Another important factor is that, along with quality, the preparation of ABM using SBS binders is more economically profitable than the above-mentioned PBA. EVA polymer changes the rheological properties of road bitumen and has a positive effect on the water, crack and shear resistance of asphalt concrete. Carbon nanotubes act as a cross-linking agent, and the use of such modified binders in asphalt concrete mixtures helps to increase water resistance, shear resistance and tensile strength.

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