Improving the quality of asphalt coating with carbon nanomodifiers

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Abstract. This article deals with the possibility of modifying the binder by adding carbon nanomodifier to bitumen to improve the quality of asphalt. Addition of 0.05%-0.5% of nanomodifier significantly changes the properties of bitumen. Asphalt with this astringent has increased strength, heat resistance and shear resistance.

1. Introduction

One of the main reasons why pavement is breaking before its time is the poor quality of road bitumen. Bitumen does not have adhesion characteristics, which are necessary, because it agglutinates only mineral pieces of basic species. Beside that bitumen becomes fragile during severe winters in Russia. In sharply continental climate of the Republic of Buryatia the amplitude of the temperature fluctuations is very high, both annual and daily. Also cold and snowless winter may start very abruptly and maintain for a very long time. These circumstances lead to a formation of cavities on pavements, which, considering the low strength of asphalt, transform into potholes [1].

According to that, the problem of increasing the quality of road bitumen is becoming an urgent issue, and the solution of it will help to maintain terms of pavement usage and to increase efficiency of its building and reparation.

For managing the process of bitumen structure formation with specific parameters (distribution of different fractions of bitumen according to thickness of its adsorption layer) a variety of modifiers is being used, both organic and mineral compounds. These compounds are working in different ways: first, formation of the polymer “grid”, which is responsible for increasing the interval of flexibility, or second, enlargement of quantity of active centers on mineral part surface, which can take part in chemical reacting with bitumen (chemisorption). The first method is provided by adding different organic compounds, such as rubber, polymeric additives, their combinations, etc. The second technique is implemented by other agents, such as phosphoric acid or hydrochloric acid. Different nano additives like nanotubes, fullerenes, astralenes and nanodiamonds compose a separate group of agents which performance is poorly investigated [2].

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A number of scientists were studying the effects of adding carbon nanomodifiers into bitumen. Thus, in one of the works carbon nanotubes (CNT) were chosen as a modifier, in amount of 0.005% of bitumen weight. Oil bitumen modifying is implemented by using ultrasound. Increased strength, flexibility as well as water, heat and cold resistance are found as a result of adding the carbon nanomodifiers in asphalt concrete[3].

In the other work, as a modifier for asphalt concrete, carbon nanotubes were used in amount of 0.2%-10% of bitumen weight. Technical result of the work is obtainment of high wear resistance and durability of bituminous concrete[4].

Authors of another work applied "Taunit" as a modifier, which is dimensional nanoscale filamentous formations of polycrystalline carbon, represented as loose black powder, which was used in amount of0.01- 0.001% of bitumen weight. Using of this modifier makes positive impact on durability and stability of bituminous concrete[5].

Researchers are paying more attention to modifying of bitumen with CNT and nano-sized carbon black, when, at the same time, the impact of fullerenes on bitumen qualities is not well discovered.
The main goal of this work is to study the influence of carbon nanomodifiers (CNM) on road building materials exploited in sharply-continental climate.

This work deals with the asphalt concrete using bitumen, modified by CNM. The authors defined basic physical, mechanical and deformation properties of that concrete.

2. Material and methods

Synthesis of initial carbon nanomodifier were carried out on the special apparatus - a plasma-chemical reactor (figure1).

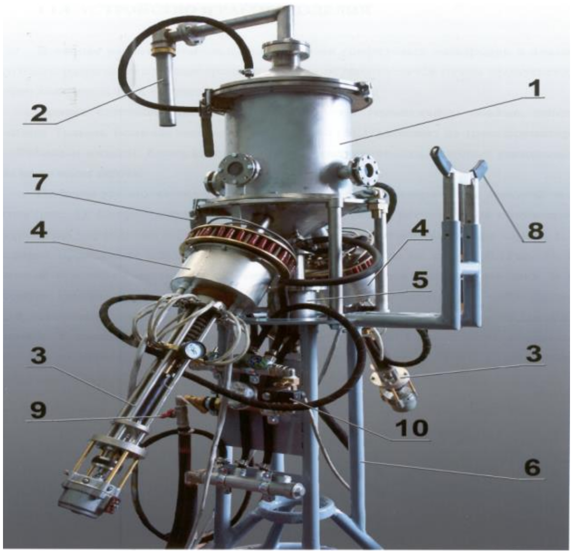

Figure 1. General view (plasma chemical reactor): 1 - camera for the synthesis 2-nitrogen trap, 3 - stocks, 4-block to meet the load, 5-carbon condensate storage device, 6-rack, 7-clips, 8-detent, 9-tap, 10 - the valve controlling the supply of cold water.

Apparatus were successfully tested previously for the synthesis of fullerene mixture at preparing targets, sputtered by ion beams and evaporated by electron beams. Targets were used in the synthesis of fullerene derivatives coatings [6].

The principle of the system is based on the erosion of graphite electrodes in the arc discharge plasma [7]. The discharge is initiated at a pressure of 105 Pa, by passing through the electrodes with current frequency 44 or 66 kHz. Erosion of rods occurs in a closed sealed volume, filled with helium.
The synthesis of plasma is taking place in the water-cooled chamber 1 of the apparatus. Towards the bottom and the top of the chamber nitrogen traps 2 are mounted through the flanges. There are inspection windows provided in the chamber for visual observation. The chamber caps are removable. Stocks 3 are attached to the removable bottom part of the chamber. There is a system which provides their movement according to rods combustion, along with coordination system with load 4.Synthesized carbon condensate is collected from the chamber walls in the store 5. Chamber is

located on the rack 6. Electric power is supplied from the voltage generator with a rated capacity of 16 kW. Maximum amperage of erosion of graphite rods is 160 A. The average time of synthesis is 10 min. Fullerenes were selected by benzol from carboncondensatecontaining10-12% of fullerenes.CNM contains parts by weight: 0.8 - C60; 0.15 - C70; the rest of it - higher fullerenes and oxides C60O and C70O (figure 2).

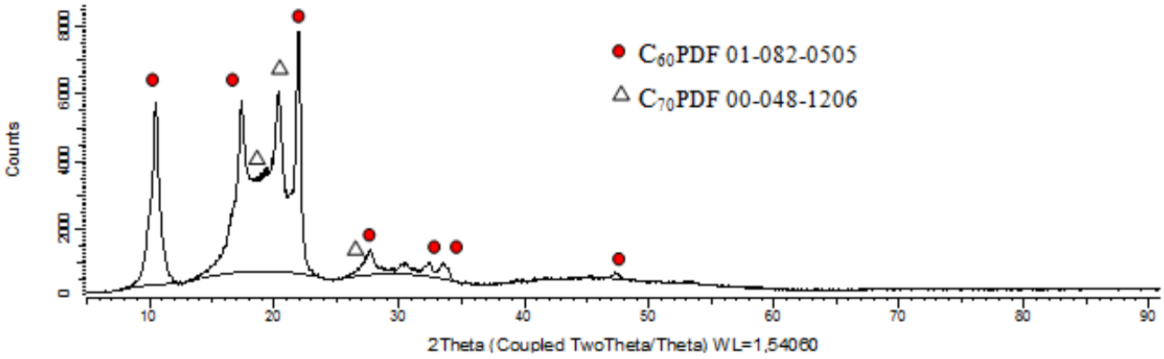

Figure 2. - XRD pattern of CNM.

Bitumen of grade 90/130 was used to determine the properties of the binder. For the preparation of bituminous mixtures the following materials were used: crushed granite, granite screenings of crushing with grain size of up to 5 mm, river sand with a fineness modulus Mk = 3 and mineral powder MP-1 - ground limestone.

Basic properties of the original and CNM modified bitumen were defined using standard test methods: the temperature of softening by the “ring and sphere” method was determined according to the StSt 11506-73, penetration was determined according to the StSt 11502-82.
The properties of original and CNM modified bitumen, BND 90/130, are shown in table 1.

Table 1. Properties of the original bitumen and the bitumen modified by CNM.

Name index bitumen	Initial bitumen BND 90/130	Bitumen + 0.05 % mass CNM	Bitumen + 0.1 % mass CNM	Bitumen + 0.25 % mass CNM	Bitumen + 0.5 % mass CNM
Penetrationat 25 ℃, 0.1mm	95	90	81	78	62
Temperature of softening, ℃	46	45	43	42	40

In order to evaluate the impact of CNM on the quality of the binder, the samples of asphalt concrete mixtures were prepared according to the recipe in the table 2.

Table 2. Composition of the fine-grained asphalt mixes of the type B, brand 2 for a road-climatic zone1 (Siberian Region).

The name of asphalt component	Content by mass, %
Crushed stone from quarry "Vahmistrovo". Fractions 15-5 mm	44
Crushed sand, fractions 5-0mm	48
Mineral powder [a]	8
Organic binder [b] (Over 100 %)	5.6

[a]The limestone powder was used as a mineral powder.
[b]The organic binder – bitumen modified by additives used in this study.

The introduction was made by heating the bitumen to 140ºC with mechanical stirring of CNM. In addition, the authors investigated the possibility of obtaining steady suspension of CNM in an organic solvent - toluene, with further introduction in bituminous concrete mixture. Moreover, the formation of bituminous concrete microstructure with strong aggregates adhesion with organic binder was taken into account. Determination of durability characteristics were carried out according to StSt 12801-98. Experimental bitumen compositions and methods of administration of CNM are presented in table 3. The results of CNM amount optimization studies are shown in tables 4, 5 and figures 3-6.

Table 3. Methods of dispositions of modified bitumen.

Composition	Distribution method CNM with binder	Quantity CNM by weight bitumen, %
1	-	0
2	Mechanical Mixing by 140ºC	0.05
3	Mechanical Mixing by 140ºC	0.1
4	Spreading CNM in toluene	0.1

3. Results and discussion

According to the table 1, it is clear that the introduction and increasing the number of CNM decrease the temperature of bitumen softening. Reducing the viscosity of bitumen in the process temperature promotes better wetting of the surface of the stone material - aggregate organic binder.

Possibly, resins, which are responsible for the bitumen plasticity, exhibit their properties much better by interacting with fullerenes. At the same time, the depth of the needle penetration is reduced, so bitumen turned up stronger. Hence, the asphaltenes, which determine the degree of bitumen hardness, also interact with fullerenes. That is to say, bitumen acquires new unique properties by administering CNM.

During the development of the asphalt composition using the modified bitumen the authors had a few tasks. They defined an optimal content and composition of CNM depending on the composition of electrode, used in the preparation of a modifying additive. Also the authors determined the method of introduction of CNM in bitumen, providing more evenly distributed nano-dispersed additive in the organic binder.

Table 4. Physical and mechanical parameters of organic compounds on the basis of bitumen, modified with CNM, identified by the StSt 12801-98 methods.

Number of the sample in the Table3	Average density, g/cm^3	Breaking point at compressing specimens, MPa			Water resistance index	Watersaturation in volume, %
		$R_{50℃}$	$R_{20℃}$	$R_{0℃}$		
1	2.37	0.91	2.53	4.31	0.94	3.22
2	2.38	1.05	2.5	4.13	0.95	2.98
3	2.39	1.53	2.75	4.37	0.98	2.31
4	2.37	1.21	2.53	4.55	0.97	2.29
Requirements of the StSt 9128-97		Least 0.9 MPa	Least 2.2MPa	Not more 10MPa	Least 0.9	1.5%-4.0%

Table 5. Thermal and mechanical parameters of organic compounds on the basis of bitumen, modified with CNM, identified by the StSt 12801-98 methods.

Number of the sample in the Table3	Heat resistance index, R_{50}/R_{20}	Temperature sensibility index, R_{50}/R_0	Calculated crack resistance, R_0/R_{50}	Shear resistance:	
				Internal attrition index	Adhesiondisplacement,MPa
1	0.36	0.21	4.73	0.87	0.32
2	0.42	0.25	3.93	0.82	0.35
3	0.56	0.35	2.85	0.85	0.43
4	0.48	0.27	3.76	0.88	0.37

The analysis of the results showed that CNM modified asphalt has a higher streng that 20°Cand 50°Candincreasedwaterresistance. The compressive strength of specimens of asphalt concrete with the introduction of 0.1% of CNM at 20°C has increased by 10%, at 50°C –by 70%, with adding of 0.05% of CNM - 5% and 15% respectively. One can see a significant increase in strength at 50°C, especially by administering large amounts of nanomodifiers- 0.1%.

CNM dissolution in toluene showed no significant changes in the properties of asphalt, compared to the introduction of the original additive in hot bitumen.

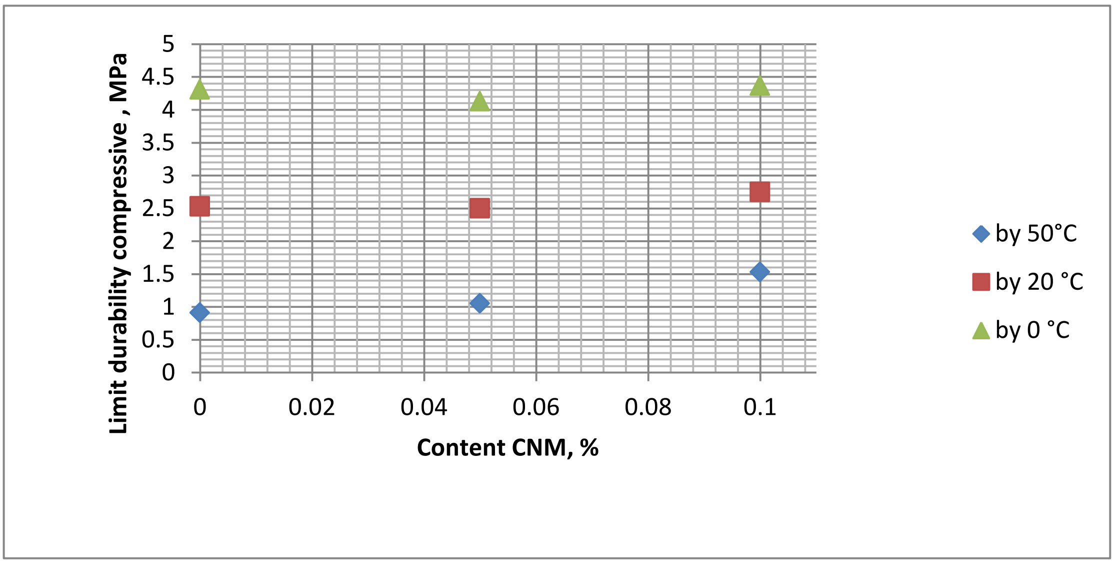

Figure 3. Characteristics durability bituminous concrete by different temperatures.

Increasing in strength can be explained by improving of bitumen structure, using carbon nanomodifers. Hence, binder can be more efficiently transferred from the bulk to the pellicle condition. Consequently, asphalt strength is increased at the 50°C and slightly decreased at 0°C. Therefore, the use of CNM modified bitumen will improve important performance characteristics such as heat resistance and shear resistance.

Analysis of the results showed that the optimum amount of CNM additive in the asphaltic mixture is equal to 0.1% by weight.

The temperature range, in which the asphalt remains in the elastic-plastic state, can be characterized by the temperature sensitivity index, which was calculated as the ratio of strength at 50°C to the strength at 0°C.

Results, presented on a figure 4, show the increasing of temperature sensitivity index as a result of the introduction of CNM: with the introduction of 0.05% - increasing by 19%, with the introduction of 0.1% - by 66%. This can be explained by decrease in the amount of bitumen in the bulk condition and more complete transfer of it into a structured condition, therefore asphalt will remain in the elastic-plastic state at greater temperature range, will be less exposed to cracking and will resist greater amount of temperature fluctuations.

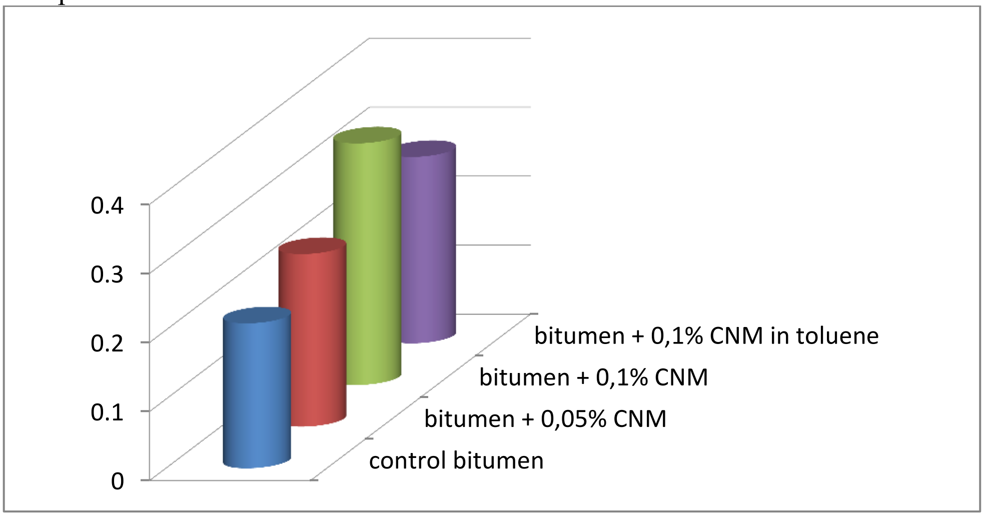

Figure 4. Change index temperature sensibility adding CNM.

The resistance of asphalt to stress at high temperatures is characterized by a heat resistance index. The results show a signifi cant increase of asphalt thermal resistance index. With the introduction of 0.05% CNM this parameter increased 1.16 times, the introduction of 0.1% - 1.55 times (figure5), which will reduce the risk of plastic deformations.

Resistance to the formation of waves, in fluxes and other shear deformations is characterized by the asphalt shear strength. This parameter is determined by the test of the Marshall method. The results, presented on figure 6, show the increase of asphalt shear strength using bitumen, modified with 0.1% CNM, by 34%. This is obviously duet enlarged cohesive strength hand viscosity of the modified bitumen. All this will create asphalt concrete with high strength and high shear resistance[8].

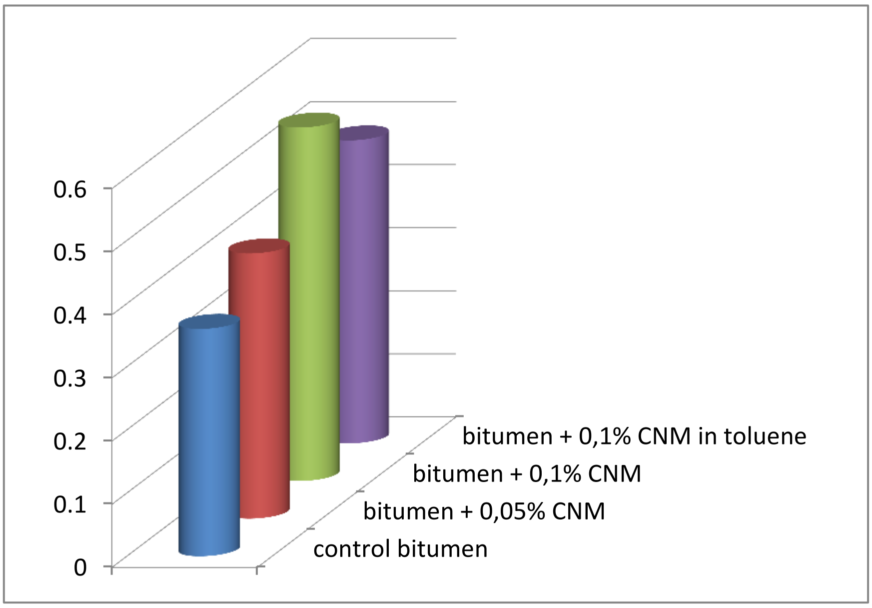

Figure 5. Change index heat resistance adding CNM.

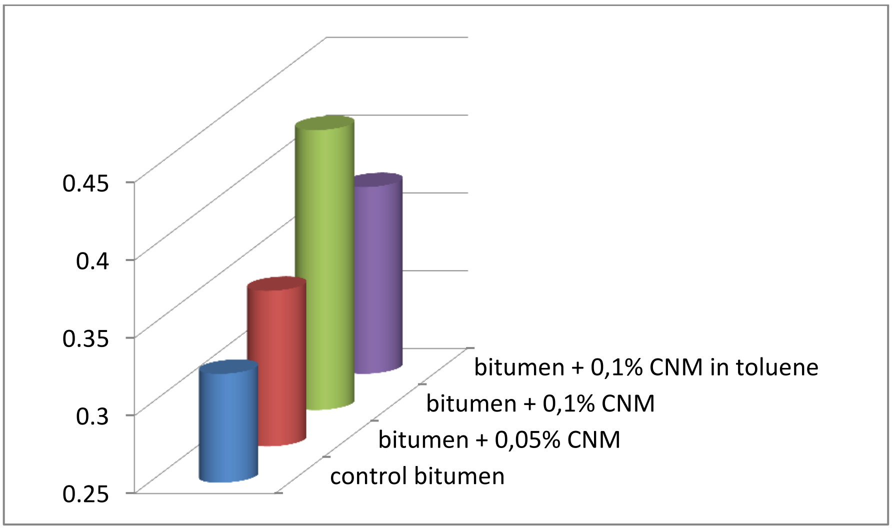

Figure 6. Change adhesion displacement bituminous concrete adding CNM.

From the literature it is known that asphaltenes make bitumen harder and heat resistant, resins determine its plasticity and flexibility, and oils have a plasticizing effect. Therefore, it can be assumed that aromatic and polycyclic structures of asphaltenes and resins, which include nitrogen heterocycles and sulfur, and have a π-bond and atoms with no divided electronic pairs, when interacting with CNM, can form strong structural clusters. Because of the spatial volume of the fullerene molecule cluster growth is happening throughout the entire volume of binder and, intertwining, forms a strong and rigid spatial network, which is increasing the hardness and heat resistance of bitumen.

The molecules of organic substances in bitumen are complex and contain a wide variety of functional groups. It can be as summed that the contact between the fullerene molecules and bitumen compounds will form strong bonds. In cases when there are several points at which the molecules are joined, even through the hydrogen bonds, to the surface, the desorption of substance is substantially irreversible [9]. At higher concentrations of CNM in bitumen there is a growth of clusters centers and, therefore, growth and density of the polymer matrix formation, which, in its turn, increases the strength characteristics.

4. Conclusions

With modifying bitumen by CNM the properties of a binder are changing, that leads to improved properties of the asphalt. Yet little studied and mastered, with small dosages modifiers significantly change the properties and structure of road materials and coatings based on them. Thus, CNM can be regarded as an effective modifier, and this direction of road-building materials science is extremely promising.

Acknowledgments

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