Nanotubes as a Modifier Polymer Modified Binder and Asphalt Concrete

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***Abstract*. New method of quality improvement of the polymer modified binder (PMB) was considered in the paper. Testify to the fact that PMB modified by nanoagent is less sensitive to aging, as a result of the processes of peptization asphaltene-resin complexes (ARC) in the structure of the modified binder and the crosslinking with the polymer matrix. It is demonstrated that the nanotubes, (SWCNT or MWCNT) using as a modifier, have effect of crosslinking agent and the inhibitor of the aging process of a PBB. The influence of nanomodified PBB on strength and deformation properties of asphalt concrete is researched. It is found that the application of modified binder in the asphalt concrete mixtures enhances the water resistance of asphalt concrete, heat resistance, and shear resistance.**

Keywords—nanotubes; polymer-bitumen binder; cross-linking; and inhibitor of aging; polymerization; water resistance; heat resistance; shear resistance

I. Introduction

In modern society, nanotechnology is an integral part of a successful and progressive development in all spheres of mankind's activity. Materials science is not exception. Analysis of innovative development of construction technologies and materials demonstrates that the materials and technologies based on nanoscale technology will be in use for the next 10-20 years. [1-2]. Nowadays, the application of nanotechnology composites to enhance functional properties of building materials and products – is a promising new direction in science and science-intensive production.

However, asphalt concrete is the main construction material in the current situation. Nevertheless, asphalt concrete usually has low crack resistant, shear-resistant and wheel track rutting resistant. This is due to their sensitivity to temperature fluctuations of the external conditions as sources of continuing structural changes occurring in conjunction with mechanical effects from the traffic stream. These influences continuously change the plasticity of asphalt concrete and its binding part, and become the reason of the structure destruction – formation of cracks and to the loss of stability of deformation – shifts, sagging, rutting.

Great number of works dedicates by improving the quality of asphalt pavement [3-5]. The literature review shows that the most promising direction in this area is modification of raw materials and organic binders. Taking into account key structural role of bitumen in the asphalt composition and a rapidly increasing load on the road pavement, it is necessary to use system principle of the improvement of the organic binders quality. This results can be achieved by improvement the properties of bitumen using various modern modifiers or their combination: polymer additives, antioxidants, nanomodifiers, surfactants, cross-linking additives [3-5], or their complex use. Researchers have heighten interest in nanostructured additives [6, 7]. This method allows possibility to create technologies and materials of new generation.

II. Objects and methods of research

The paper is dedicated to the impact of different carbon nanotubes on the properties of organic binders and asphalt concrete. Subjects of research are: initial material of single-walled carbon nanotubes (SWCNT), multiwall carbon nanotubes (MWCNT), representing a one-dimensional nanoscale filamentary formations polycrystalline graphite in the form of loose powder, bitumen 90/130, thermoplastic elastomers class polymer, a plasticizer.

Studies performed earlier [8-10] are demonstrated the effect of the application of nanotubes in the preparation of PBB. Based on this knowledge, the most rational and efficient composition of the PMB were chosen, and preparation technology was created [9].

III. Research

A. Effect of nanotubes on polymer - bitumen binder

For testing theoretical assumptions and derived relationships, pilot industrial samples were prepared: SWCNT modified (composition No. 1), MWCNT (composition No. 2) and the control series - without nano modifier. The binder compositions are shown in Table I.

TABLE I. Compositions of industrial design PMB

Composition. %	**item No.**		
	No. 1	***No. 2***	***No. 3***
Nano modifier	$1\ 10^{-5}$	$5\ 10^{-5}$	-
Polymer	3,2	3,2	3,2
Plasticizer	1,8	1,8	1,8
Bitumen	rest	rest	rest

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Research of the nanotubes influence are included standard indicators of the quality of nanomodified PBB, their resistance to delamination and aging (Table II). The influence of the derived PMB on the quality of asphalt is listed in the Table III.

During the examination the quality indicators of the WSP, it was found that the control binder No. 3, prepared without nano-modifier, does not meet the requirements [11] against the following parameters: softening point, penetration (viscosity) at 0 ^{0}C, the extensibility and elasticity at 0 ^{0}C. Beyond that a phase separation tendency is observed, which indicated low content of the polymer required for the formation of lasting spatial polymer network. As a result this sample can be characterized as a material of unsatisfactory quality.

TABLE II. COMPOSITIONS OF INDUSTRIAL DESIGN PBB

Indicator name	**Requirements document**	**item No.**		
		No. 1	***No. 2***	***No. 3***
peelability in a tube: - low temperature brittleness, ^{0}C, up/down tubes, - the softening temperature, ^{0}C, up/down tubes ,	- 5	-26/-24 75/75	- 27/-27 73/70	-28/-20 56/43
low temperature brittleness, C	-20	-24	-28	- 20
the softening temperature, ^{0}C	54	73	62	51
uniformity	uniformity	unifor-mity	unifor-mity	unifor-mity
penetration, 0.1 mm, 25^{0}C/0^{0}C	60/32	74/34	72/33	68/28
expansibility, cm, 25^{0}C/0^{0}C	25/11	75/21	87/23	65/10
elasticity, % , 25^{0}C/0^{0}C	80/70	95/93	95/94	92/43
aging resistance TFOT - change in mass, % - changing the softening temperature, ^{0}C	- -	0,05 1	0,05 1	1,5 11
cohesive strength , kgp/cm	-	13	14	9

However, the binders prepared in a similar way to sample No. 3, but with the adding of the nanomodifiers, have significantly higher characteristics and meet the requirements of GOST and EN in all parameters. Especially it is necessary to emphasize following important indicators: resistance to delamination and aging.

Index of peelability of the modified binders is measured at the difference embrittlement temperature up/down of the tube, after the test amounted 2^{0}C for samples series No. 1 (SWCNT) and 0^{0}C for samples series No. 2 (MWCNT). The softening temperature after warm-up PBB in tube is changed 0^{0}C (SWCNT) and 3^{0}C (MWCNT) that characterizes series No. 1 and No. 2 as binders of high quality, with high resistance to delamination. Aging resistance is an important indicator, which simulating the resistance of the binder to oxidative processes at high temperatures. It is determinated by two indicators: changing in weight (volatilization of light fractions - embrittlement of binder) and changing the softening temperature after warm-up. Table II is shown minor variation of these parameters of nanomodified binders, unlike control sample.

B. The study of the processes of structure formation in the binder

As may be supposed the results of high resistance to aging and peelability from nanomodified WSPs are explained by processes occurring at the micro - and nanolevels. Ultrasound using for the adding of nanotubes in the bituminous matrix [9], allows to break agglomerates of the nanotubes is a tangled balls of various sizes, in which hundreds of carbon nanotubes interconnected by the van der Waals forces. As a result, tubes are distributed regularly in volume, and are increased specific surface area significantly. Obviously, nanoobjects, included in the PMB, are built into the structure of asphaltene-resin complexes (ARC) like bridges. They connect the dispersed aggregates of asphaltene and polymer molecules. As a result, convergence of the particles in the bitumen – polymer matrix become possible.

This assumption confirms by the study asphaltene-resin complexes (ARC), deposited from modified binder and a control sample, using electronic field emission microscope ZEISS LEO SUPRA 25. Result are shown in Fig. 1.

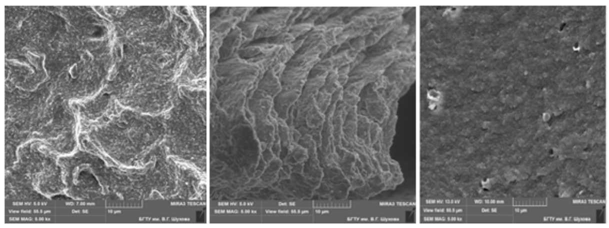

Fig. 1. *Micrograph of the structure of asphaltene-resin complexes a) composition No.1, b) composition No.2, c) composition No.3.*

Fig. 1c illustrates the microstructure ARC of the binder without nanomodification, as can be seen, the structure is homogeneous, granular, composed of the larger ARC, which resemble grapes. After adding of nanoscale modifiers SWCNT, (Fig. 1a), a peculiar effect of reinforcement is appeared, the nano-objects is structured around the ARC, their size is reduced. The structure is characterized by the relief surface, which, obviously, can slow the aging process and minimize separation processes PBB in combination with the characteristics of the structure of the ARC mentioned above. Adding of the modifier MWCNT, Fig. 1b, is formed a "comb", the layered structure without pronounced grain, which also has a positive impact on the performance properties of the binder. It can be assumed, that, due to the structuring of the ARC by the nano-objects at the modified binder, cohesive strength and elasticity indicators, which are responsible for intermolecular interaction, are increased. Obviously, the nanotubes play role of an inhibitor of aging and a cross-linking agent. It occurs as a result of the processes of reducing the size of asphaltene-resin complexes in the structure of the modified binder and the crosslinking with the polymer matrix. As a result, it becomes possible to obtain a PMB with effective properties.

During comparing properties of nanomodified PBB, following consistent pattern was determined. SWNT has a strong influence on the heat resistance of binders, and

MWCNT has an effect on low-temperature indicators, which improved complex of properties of the asphalt concrete.

C. *Effect of nanotubes on asphalt concrete*

Mineral part of asphalt mix type B, mark I was designed for assessment of the impact of WSP series No. 1 - No. 3 on the properties of asphalt concrete.

Based on selected mineral composition, testing asphalt samples were prepared and physical and mechanical properties were studied. The results of the study are presented in Table III.

TABLE III. PERFORMANCE PROPERTIES OF POLYMER ASPHALT CONCRETE TYPE B MARK I

Indicator name	**Requirements document**	**item No.**		
		No. 1	***No. 2***	***No.3***
water saturation, %	1,0…2,5	1,6	1,8	1,87
average density	-	2,41	2,41	2,41
limit of compressive strength, mPa:				
+20^{0}C	>2,0	4,02	3,90	2,54
+50^{0}C	>1,1	2,95	2,80	1,91
0^{0}C	<9,0	8,7	8,3	9,2
water resistance	>0,9	1,10	1,01	0,90
long water resistance	>0,85	1,05	0,99	0,82
heat resistance	-	1,46	1,40	1,30
sensitivity to temperature changes	-	2,16	2,12	3,62
limit of tensile strength at the split, 0^{0}C	2,8-6,0	3,85	3,80	2,81
shear resistance:				
- coefficient of internal friction	0,81	1,14	1,01	0,92
- clutch when shifting	0,3	0,97	0,86	0,61

As can be seen, application of nano-modified binder in the composition of polymer asphalt concrete mixes contributes to a significant improvement of the water resistance and deformation resistance of asphalt concrete. The indicator of water resistance of samples in series No. 1 and No. 2, without additional adhesive and crosslinking additives, is increased by 20% and 12%, respectively, in comparing with control series of binders. A more pronounced change in the water resistance of PMB is observed after a long period of water saturation. Thus, the indicator of long-term water resistance of samples in series No. 1 (SWCNT) is reduced by 4.5%, series No. 2 (MWCNT) by 2%, while for the control series No. 3 this parameter is reduced by 9%. Thus, the results are characterized the obtained nano-modified polymer asphalt concrete, as a composite with increased resistance to aggressive effects of rainfall and wastewater.

Also, the resistance of nano-modified polymer asphalt concrete significantly increases, sensitivity to temperature changes is reduced, and it becomes possible to regulate the strength characteristics of the composite. During the experiment, the assumption mentioned above, about the differentiated impact of nanotubes SWCNT and MWCNT composites on road, was confirmed, as the Table III shows.

Based on the research results, following conclusions can be created. Polymer asphalt concretes created with nano modifiers have significantly improved performance indicators, contributing to significant extension of service life of pavement road surface from asphalt concrete without premature failure, which would make the road safer for all road users.

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